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HYDROGENATION OF NITRO-COMPOUNDS OVERRHODIUM CATALYSTS SUPPORTED ON POLY[ACRYLIC ACID]/Al₂O₃COMPOSITES

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HIGHLIGHTS

- New well-defined hybrid composites from acrylic acid polymer with Al₂O₃
- Rhnanoparticles and di-rhodium carboxylate complex deposition on PAA/Al₂O₃ supports.
- Metallic Rh using as catalysts in nitro-compounds hydrogenation.
- Upper 98% selectivity was achieved over all the catalysts for nitrobenzene hydrogenation
- Reaction over the most selective catalystshowed a linear Hammett relationship and positive reaction constant ($\rho = 1.24$).

ABSTRACT

In this report, poly[acrylic acid] gels containing Al₂O₃ were prepared by simultaneous freeradical polymerization and sol-gel chemistry using different amounts of 3-(trimethoxysilyl)propyl methacrylate (TMPM) as acompatibilizer. The hybrid materialswereused assupports for arhodium catalyst in the chemoselectivehydrogenation of 3-substituted aromatic nitro-compounds. The supported rhodium catalyst was prepared by an ion-exchange process. In situ H₂ flux was used to produce active species of the catalysts. The resulting materials were characterized by infrared spectroscopy, thermogravimetric analysis, solid-state ²⁹Si and ¹³C 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 -NO₂ group reduction, resulting in the sole formation of the corresponding amino-compound, with the exception of1,3-dinitrobenzene, in which over-hydrogenation was detected. The presence of electrondonating/electron-withdrawing substituents at the 3-position resulted in different rates of – NO₂grouphydrogenation. 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, -NH₂, and -OCH₃ groups. One explanation for this behavior is a proposed support-substrate hydrogen bond interaction during the catalytic reaction.

Keywords: Rhodium, hybrid materials, hydrogenation, metallic catalysts.

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 theirpotential forapplication 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 andthe 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 polymericinorganic 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 beimmiscible. 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 endsfor 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 commonly used as protecting are agents. such as poly[vinylpyrrolidone] (PVP)[6, 26], poly[vinyl alcohol] (PVA)[6]andpoly[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 materialsperform 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/Al₂O₃ 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-compoundswas investigated and the catalytic data weresubjected to Hammett treatment.

2. EXPERIMENTAL SECTION

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 (RhCl₃·xH₂O; 99.98% trace metal basis), 1-chloro-3-nitrobenzene (NB-Cl; 98%), 1,3-dinitrobenzene (NB-NO₂; 97%), nitrobenzene (NB), and 1-methyl-3-nitrobenzene(NB-CN) were obtained from Sigma–Aldrich[®] and Fluka[®]. Aluminum tri-*sec*-butoxide(TSBAl; 97%), acetylacetone(acac), absolute ethanol,1methyl-3-nitrobenzene (NB-CH₃),1-methoxy-3-nitrobenzene (NB-OCH₃) and 3nitrophenol (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 N₂ atmosphere. H₂ (99.99%) was supplied by AGA[®] - Chile.

2.2 SIHN synthesis

TSBAI (0.03mol) was dissolved in anhydrous 2-butanol and heated at353K. Subsequently, 0.04 mol of acac, 0.02 mol of AA, and 0.002 mol of APS were added to the reaction mixture. TMPMwas added in different mole ratiosofTMPM/(TMPM+TSBAI):0, 0.5, 0.25 and 0.125. The reaction was carried out at 353 K under an N₂ 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 8h at room temperature and later dried in a vacuum oven at 353K 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 373K. All materials obtained were labeled as PAA/Al₂O₃—TMPM(x), where x corresponds to the TMPM/(TMPM+TSBAI) mole ratio.

2.3 Synthesis of Catalysts

The catalysts (1.0 g) were prepared at 0.5wt% Rh using PAA/Al₂O₃-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 molL⁻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 RhCl₃xH₂O was added to obtain the desired metal loading,and the system was placed in a thermoregulated bathfor 12 h at 318K withmagnetic 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 N₂ atmosphere prior to the catalytic tests. These were labeled as 0.5%Rh-PAA/Al₂O₃-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 Perkin Elmer Elas 6000S instrument. The morphological and structural characteristics of the composites and catalysts were determined by XRD (RigakuD/max-2500 diffractometer with Cu K_α 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 ¹³C and ²⁹Si 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 N₂ atmosphere.N₂-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 (CaCO₃), Si and O (SiO₂), Al (Al₂O₃), S (FeS₂). The transmission electron microscope was carried out in a Philips model CM200 equipment with an energy dispersive analyzer and a digital camera coupled to a high speed TVIPS (FastScan F-114 model)at 1024x1024 pixels and 12 bits. The samples for analysis were prepared by dispersion in ethanol/H₂O (1:1) and deposited on a porous carbon/Cu grid (300 mesh). Up to 300 individual metal particles were measured for each catalyst and the surface area-weighted mean Rh diameter (d_p) was calculated using:

$$d_p = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

Wheren_i is the number of particles of diameter d_i . The size limit for the detection of Rh particles on samples was ca. 1 nm. Assuming a population of monodispersed (i.e., with the same size) metal particles, the dispersion, D (%), is related to the mean particle size by a simple formula:

$$D(\%) = \frac{1.09}{d_p(nm)} \cdot 100$$

where D corresponds to the ratio of the number of surface metal atoms to the total number of metal atoms[32]. X-ray photoelectron spectra (XPS) were recorded using an Escalab 200 R spectrometer equipped with a hemispherical analyzer and using non-monochromatic Mg K α X-ray radiation (h ν =1253.6 eV). The spectra were fitto a combination of Gaussian-Lorentzian lines of variable proportion. The C 1s core-level of adventitious carbon at a binding energy (BE) of 284.8 eV was used as an internal standard.

2.5 Catalytic activity

Catalytic activity assays of the hydrogenation of 3-substituted aromatic nitro-compounds were performed in a stainless steel, Parr-type batch reactor at a concentration of 0.02 molL⁻ 1 of substrate using absolute ethanol as a solvent and stirring at 800 rpm under 20 bar H₂ pressure at 298K. All further experiments were carried out in the absence of external mass transfer limitations[33]. The tested catalysts were in the form of a fine powder (>30 µm).For the substrate/Rh molar ratio studies, the concentration of substrate was kept constant and the mass of the catalyst was varied.Small differences in initial velocity were observed in the range of catalyst mass studied (0.01-0.07g) because the reaction rate was proportional to the catalyst mass. In these studies, 0.050g of catalyst was used for kinetic measurements. A non-invasive liquid sampling system with an in-line filter allowed the controlled removal of aliquots (≤ 0.5 cm³) from the reactor. All the catalytic experiments were made three times (with fresh catalyst every time) and the average values were reported for kinetic data. The samples of reactions were analyzed in a GC-MS Shimadzu (GCMS-QP5050) with helium as the carrier gas was used to analyze the reactants and products. The turnover frequency (TOF) of the catalysts was calculated using:

 $TOF(s^{-1}) = \frac{Substrate\ hydrogenated\ (mol)}{Surface\ metallic\ Rh\ (mol)\cdot\ time(s)}$

3. RESULTS AND DISCUSSION

3.1 Support Synthesis and Characterization

A washing procedure was performed to remove unreacted monomer and impurities in the material. ThePAA/Al₂O₃-TMPM(0) composite resulted in the lowest yield (56%); this result can be attributed to the absence of the coupling agent. For the compositesPAA/Al₂O₃-TMPM(x) with x > 0, the yieldincreased as the TMPM content increased (x: 0.125, 58%; x: 2.5, 61% and x: 0.5, 75%) because it acts as a crosslinking agent between Al₂O₃ and the PAA chains.

Figure 1 displays FT-IR spectra of PAA/Al₂O₃-TMPM(x). The expected absorption bandsfor the silicon compounds areobservedat 1113 cm⁻¹ (C–Si–O, st). The absorption peak of the Al–O stretching vibration often appears in the range of 1000–1200cm⁻¹.However, for the present system,this peak could not be resolved due to its overlap with the absorption peak of the Si–O–Si stretching vibration. The absorption band at3436cm⁻¹ is associated with the O–H bond vibration, while the very strong band at 1532 cm⁻¹ is attributed to the C=O carboxylic acid stretch of PAA. Theband at 1720 cm⁻¹ corresponds to theC=O ester vibration of TMPM.

Figure 2 presents theTGA and DTGA curves ofPAA/Al₂O₃-TMPM(x). TGA (see Fig. 2.a) exhibited two stages of degradation. The first step occurred at approximately 350K and corresponds to the evolution of water. The second stepappeared at higher temperatures in the range of 620–720 K, and can be attributed to degradation of the polymer, with degradation ending at 780K. Additionally, it was observed that the mass loss depended on

the TMPM content; as the TMPM content increased, the mass loss increased. In this case, the thermal decomposition of the polymer occurred at higher temperatures, which demonstrates that PAA/Al₂O₃-TMPM(0) composites have higher thermal stabilities and slower degradation rates than PAA in all cases. However, for the PAA/Al₂O₃-TMPM(x)composites with x > 0, significant changes in the TGA and DTGA (see figure 4.b) wereobserved. Twodifferent temperatures in the mass loss steps were observed. The first step, appearing at 654 K, corresponds to chemical transformations of the Si compounds. In similar systems, TMPM has been demonstrated to generateSi_xC_yO_{4-y} species upon thermolysis[34, 35]. For this reason, these results should notbe used to express the polymer content in the composite. The second weight loss (at approximately 690–720 K), which occurredto different extents, is related to degradation of the polymer (see Table 1).

Figure 3displays scanning electron microscopy (SEM) micrographs of PAA/Al₂O₃-TMPM(x) composite samples. The morphology and size of AA/Al₂O₃-TMPM(x) composite are described by SEM, and the results are shown in Fig. 3(A) - (D). The hybrid particles exhibit a layered structure with a smooth surface. The SEM images of PAA/Al₂O₃-TMPM(0) show a regular distribution of particles size. As the coupling agent content increases an increment on micro-particle size was detected. This effect can be explained for the uniformity provided by the TMPM. The polymers chains and metal oxide network shows a higher interaction in the hybrid materials in presence of coupling agent. The PAA/Al₂O₃-TMPM(x) particles obtained at higher nominal contents of TMPM are out of shape, with a regular-uniform higher size (Fig. 5(D)), in agreement with the N₂ isotherm and S_{BET} characterization.

The composition of PAA/Al₂O₃-TMPM(x) composites was quantitatively determined by EDS analysis (Fig. 5(E)-(F)) is shown in Table 2. The result clearly confirms the presence of Al and C on the surface of all the hybrids materials. Only for the PAA/Al₂O₃-TMPM(x) with x > 0, Si atom was detected.

Moreover, the weight percentages of C and Al were approximately 64% and 1-2%, respectively. These indicated that Al_2O_3 oxide phase was covered completely with PAA and the -COOH pending groups are on the surface of hybrids materials. On the other hand, Si was detected on PAA/Al₂O₃-TMPM(x) with x > 0, attributed to the TMPM in the polymer backbone and provided bridges points during the sol-gel synthesis, improving the metal oxide coating. The weight percentage of Si was lower than the nominal value. This result indicates that Si atoms are strongly associated on the metal oxide network.

All the characterizations indicate that the composites are SIHN materials because the incorporation of TMPM promotes the formation of laminar sites, which are characteristic of this type of resin materials and are consistent with the decreased surface areas, as detected by the S_{BET} results (vide infra).

3.2 Catalyst Synthesis and Characterization

The metal loadings shown in Table 3 are in the range of 0.45- 0.50 wt %. In general, the composites displayed a high adsorbed affinity for Rh(III) during the catalyst preparation process.

The FT-IR spectra, TGA, XRD,andN₂ adsorption-desorption isotherms of the supports and catalysts did not show significant differences, and the crystalline nature of the catalystswas

studied by XRD (see Fig. 4). The powder X-ray diffraction patterns of the PAA/Al₂O₃-TMPM(x)catalysts exhibited characteristic spectral profiles of amorphous aluminates with two amorphous halos present in the $2\theta = 23$ and 40° [17, 36]. This typical halo results from the dispersion of the angles and bond distances between the basic structural units (silicates and aluminates), which destroys the structural periodicity and produces a non-crystalline material. Slight changes in the diffraction patterns were observed with increasing TMPM content around $2\theta = 10^{\circ}$. This result confirms the assumption that PAA hybridization occurs on the solid surface without changing the structural form of the Al₂O₃ (composite PAA/Al₂O₃-TMPM(0)), but that TMPM insertion modifies the inorganic network during the syntheses. The characteristic Rh diffraction lines in the region of $2\theta \sim 39.4^{\circ}$ (plane 1, 1, 1) and 45.6° (plane 2, 0, 0) were not detected.

The N₂ adsorption–desorption isotherms of 0.5%Rh-PAA/Al₂O₃-TMPM(x) composite samples are shown in figure 5. The isotherms are similar to Type IV isotherms with H1type hysteresis loops at high relative pressures, according to the IUPAC classification, which is characteristic of amorphous and macro- and mesoporous materials[16]. The specific surface areas and pore sizes were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.The structural data for all materials are summarized in Table 3. It is clear that PAA/Al₂O₃-TMPM(0) has the highest BET surface area (140 m²g⁻¹), pore volume (0.37 cm³g⁻¹) and pore size (100 nm), indicative that it was a host to PAA before washing. The values of these properties were lower for the composites with x > 0 (see Table 3) than for composite PAA/Al₂O₃-TMPM(0); the TMPM resulted in more highly cross-linked materials (polymeric-oxide network), promoting smaller cavities and decreased S_{BET} values.

Metal cation sorption on chelating sorbents is a pHdependent process. The hydronium concentration in water can change the structural properties of ligands and the speciation of metal ions in aqueous solution. All of the synthesized catalysts were prepared by Rh(III) sorption. It is important to consider that the -COOH group is a weak acid; at pH 11 these groups are totally ionized [37, 38]. During the synthesis of rhodium nanoparticles, H₂ is oxidized to H⁺, resulting inan acidic medium that can alter the -COOH/-COO⁻ equilibrium. The stoichiometric addition of NaOH to the synthesis system allowed us to obtain the maximum ion-exchange/complexation process for rhodium retention and a neutral medium at the end of the nanoparticle synthesis process (approx. pH = 7.0). The metal particle sizes shown in Table 3were determined by TEM and can be observed in the micrograph shown in Figure 5. The catalyst prepared on PAA/Al₂O₃-TMPM(0) displayed large particle sizes, reaching approximately 4.6 nm, and a wide distribution of particle size values. The average metal particle sizes of samples prepared with TMPM displayed an inverse relationship with TMPM content. The polymeric network provided stability to the Rh clusters formed during the metal reduction, thereby allowing the formation of smallersized agglomerates. From these catalyst preparation results it is clear that a more crosslinked support isoptimal.

The chemical changes in the rhodium particles were also investigated by XPS. Table 4 gives the $Rh3d_{5/2}$ BEs for all of the catalysts under study, with the corresponding contribution to the overall signal in parentheses. It was interesting to observe the appearance of two peaks at 308.4 eV and 310.2 eV in allof the catalyst spectra. Rh $3d_{5/2}$ zero valentstates appearat 307.2eVin the 1.0%Rh/Al₂O₃ catalyst [39]. It is well known that very small metallic particles, a strong interaction of metal particles with their supports, orthe

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growth of metal nanoparticles in a –CCO⁻environment may produce a slight shift towards higher BEs.Based on thetypical binding energies for Rh(0), our values are slightly shifted (Δ BE = +1.2 eV). In the case where the Rh nanoparticles were grown in a –COO⁻ environment, the resulting complex could be covered with Rh surface layers, exhibiting a different periodicity when compared to the Rh lattice, which agrees with similar studies reported for Rh/MgO by Jin-Phillipp*et al.*[40]. The binding energies of Rh 3d_{5/2} spectral lines exhibit a single broad signal, which we suggest is due to an overlap of the two spectral lines (surface layers and lattice) because this Rh spectral line is very sensitive to the environment of the metal [11, 39-41].

A comparison of the integral intensities of these components further suggests that Rh(0)species constitute approximately 34 – 60% of the total Rh in the catalyst and that the contribution increases with increasing TMPM in the supports. The appearance of the additional band at 310.2 eVcorresponds to Rh(II) carboxylate complexesformed during the reduction process[42-45]. Overall, these XPS results clearly demonstrate the incomplete reduction of Rh species on the hybrid nanocomposite, which is consistent with previous literature reports by Karakhanov et al.[11]. The main reason for incomplete Rh reduction is most likely the high stability of the Rh – carboxylate ligand chelates formed during complexation.

With higher TMPM contents, the band attributed toRh(0) becomesvery intense, mainly due to the weakinteraction of the nanoparticles with the oxide surface of the inorganic network.0.5%-PAA/Al₂O₃-TMPM(x) with x:0 displays a more intense Rh(II) carboxylate complex contribution (66%), which can be attributed to the strong interactions between the

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Al₂O₃ and PAA networks. In the presence of oxygen and/or oxygen donors, these types of di-rhodium species can form oxygen-bridged carboxylate complexes with the general formulas $[Rh_3(\mu_3-O)(\mu-O_2CR)_6(L)_3]^{n+}$, $[Rh_2(\mu-O)(\mu-O_2CR)_2\cdot(L)_6]^{n+}$, and $[M_2(\mu-O)(\mu-O_2CR)_2(O_2CR)_2(L)_2]^{n+}$ [42]. These metal oxide – Rh complexes are the result of: (1) reactions resulting in changes in the oxidation state of the metal atom only[46]; (2) reactions involving the addition of extra electrons to terminal ligands L[42, 47]; and/or reactions resulting in changes in the oxidation state of the metal and the rearrangement of its core [47]. In our case, an increase in the (TMPM/(TMPM+TSBAI)) surface ratio in the syntheses results in a change on the SIHN surface due to the coverage of the support by Si-O-Al species. The binding energies for Rhd_{5/2} at 310 eV only exhibited a slight displacement to minor energies ($\Delta BE = 0.3 \text{eV}$). This behavior can be attributed to changes in terminal ligand electronic arrangements.

The binding energies assigned to each C 1s peaks are in agreement with accepted values for these functionalities [48]. The peak representative of the carbon (i.e., 284.8 eV) at the α position of the carboxylic acid group is assumed to include contributions from the C single bond of the PAA backbone. The binding energies at 286.7and 288.5 eV correspond to the contribution of C from the carboxylic acid groups on the surface of the support and the carboxylic acid ligands in the Rh – complex, respectively [48, 49]. The contribution of C1s for the carboxylic acid groups decreases the C=O_{PAA}/C-O_{PAA}withincreasing TMPM in the support structure, in agreement with the change in Rhd_{5/2} binding energies (see table 4).Finally, Si 2p binding energies at 101.3 eV for catalysts 0.5%-PAA/Al₂O₃-TMPM(x) with x > 0.125 were detected, which is typical of organosilicon compounds. The

preferential insertion of TMPM into the bulk structure is confirmed by changes in the intensity of this line when we used lower (TMPM/(TMPM+TSBAl)) nominal mole ratios.

The support structure and the Rh – PAA interactions were confirmed by solid-state ¹³C and ²⁹Si CP-MAS NMR of 0.5Rh%-PAA/Al₂O₃-TMPM(0.0) after metal reduction (see figure 6). Figure 6(A) displays the NMR spectra of PAA/Al_2O_3 -TMPM(x) with x: 0 to 0.50. The PAA shows signals at 178.7 ppm (C=O), 42.3 ppm (CH-), and 35 ppm (-CH₂-), which has also been reported by da Silva et al. [50]. The hybrid materials exhibit similar signals, but their intensities and shapes change with increasing TMPM in the structure of the materials. PAA/Al₂O₃-TMPM(0) shows three resonances for the -COOH groups at 183.3, 190.8 and 191.5 ppm. The first corresponds to the COOH/COO⁻ pendant groups, and the other two are attributed to $[Rh_2(0_2CR)_4]L_2$ (characteristic doublet of this type of complex), in agreement with similar results reported by Allen et al.[41]forrhodium catalysts prepared from carboxylate-modified silicapolyamine composites. Convincing evidence that the Rh forms a carboxylate complex with carboxylate-modified SIHN supports comes from the observation of²J¹³C⁻¹⁰³Rh (70 MHz) doublets with values in agreement with the typical Rh (μ -O₂CR)₂ or $(\mu$ -O₂CR)₄ complexes, as reported by Varshavskii*et al.* [45]. We detected the same signals and the same coupling constant values in all composites, but the intensity decreased with increasing TMPM in the support structure. These results agree with the two types of Rh species detected by XPS and confirm the coordination state of the Rh complex in the catalysts. The signals at ~100 ppm correspond to the quaternary carbon atoms formed by cross-links between the linear chains of PAA formed during the free-radical polymerization process. The AA/APS mole ratio was 10; the excess of initiator and the low solubility in 2butanol provides excellent conditions for reactivating the polymerization reaction during

the sol-gel process[51, 52]. The polymer backbone contains CH- and CH₂- signals at 43 and 28 ppm, which are typical chemical shifts for PAA[41, 50, 51, 53]. PAA/Al₂O₃-TMPM(x) with x = 0.125 - 0.50 displays the same type of C signals, along with new resonances at 68 and 9.0 ppm. These resonances correspond to the insertion of TMPM into the backbone of the polymer (methacrylate and propyl groups, respectively). The signals corresponding to the C=O groups displaying a different intensity and a slight shift relative to PAA/Al₂O₃-TMPM(0) because the increased TMPM on the surface forms Si-O-Al bonds, resulting in steric blockage of the carboxylate – Al₂O₃ sites. The signal at 102 ppm displaysa decrease with TMPM insertion because the cross-links between polymeric phases and the inorganic network decreases the mobility of the chains during the sol-gel process and results in more linear PAA chains. This result agrees with the change in the intensity of the signals at 43 and 28 ppm for the PAA/Al₂O₃-TMPM(x) supports with x > 0.125.

Figure 6(B) displays the solid-state²⁹Si CP-MAS NMR data of the PAA/Al₂O₃-TMPM(x) hybrids. In all supports, no residual unconverted TMPM was detected, as no peaksbetween 0 and -45 ppm were observed (TMPM should have a signal at -43.1 ppm) [54]. For the PAA/Al₂O₃-TMPM(x) hybrid, three resonances were detected between -47 and -68 ppm, which correspond to the T¹, T² and T³ anchors. The Al₂O₃ surface signals increase in intensity withincreasing TMPM in the composites. For PAA/Al₂O₃-TMPM(0.125), only T¹ and T² signals were detected at -47.8 and -59.4 ppm, respectively. The PAA/Al₂O₃-TMPM(x) composites with x = 0.25 and 0.50exhibited three types of anchors. This is attributed to the increase in the (TMPM/TMPM+TSBAI) nominal mole ratio in the synthesis, which provides more sites for the formation of Si-O-Al bonds during the hydrolysis-condensation process.

3.3 Nitrobenzene hydrogenation

Figure 7displays the activity of all catalysts used for the hydrogenation of NB. Increasing the TMPM loading in the framework of the catalyst surface improved the activity. Pseudofirst order kinetics (kg) with respect to NB was found in all cases. The turnover frequencies (TOF) are given in Table 5. The possibility that the reaction reached equilibrium during the measurements can be excluded, and all results shown are the maximum conversions before reaching equilibrium. The TOF were calculated based on conversion of NB to An. All catalysts were selective for aniline (An) and gave yields above 98%, as shown in Table 5. Products from aromatic ring hydrogenation were not detected. 0.5%Rh-PAA/Al₂O₃-TMPM(0.0) exhibited the lowest conversion of NB. These results confirm the synergistic effect of using TMPM in the preparation of the rhodium nanoparticle supports. The catalyst prepared without TMPM contained irregular Rh nanoparticles with respect to the other supports. It might be expected that this would lead to the preferential incorporation of metal inside the tunnel framework, which would improve the activity of the catalyst. However, the catalyst lacking TMPM contained a higher percentage of Rh carboxylate complexes, as detected by XPS characterization (see table 4). This type of complex does not possess catalytic activity in hydrogenation reactions [53]. Previous studies have demonstrated that this reaction is a structure-sensitive reaction [31, 55]. In fact, the ability of the support surface to disperse the metal nanoparticles results in a smaller metal particle size and improves the activity and yield in NB hydrogenations[31]. In this case, the incorporation of TMPM improves the reduction of the di-rhodium complex species remaining from the reductionprocess. Table5displays some of the kinetic parameters for NB hydrogenation andyields of An.Using Rh nanoparticles in the SIHN as a catalyst and ethanol as the solvent resulted in the production of phenyl-hydroxylamine(2 when X = H in scheme 1) and

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nitrosobenzene (3 when X = H in scheme 1) as the by-products (approximately 1-2%) (see scheme 1 proposed by Kratky et al.[56]). The 0.5% Rh-PAA/Al₂O₃-TMPM(0) catalyst resulted in aslightly loweryield of An, 98.2%, after 4 h of reaction. However, both the reactivity and selectivity was higher than for the other catalysts. The 0.5%Rh-PAA/Al₂O₃-TMPM(0.125) catalyst (containing an overall metal component of 38% and 62% dirhodium complex on the surface) resulted in a greater conversion than the 0.5%Rh-PAA/Al₂O₃-TMPM(0.0) catalystafter 7h of hydrogenation, as well an increase inselectivity (see Table 6). Thesehydrogenation yields were higherwhen compared to other reported metal noble catalysts[57-60]. It has been reported that the rate-determining step of the hydrogenation of NB derivatives is a nucleophilic attack of hydride ion, produced by dissociative adsorption of a H₂ molecule on the metal surface, on the nitrogen atom of the -NO₂ group [33, 55, 57]. The PAA on the surface of the support promotes the constant polarization of Rh nanoparticles. These active sites increase the electrophilic character of the -NO₂ group during the hydrogenation and decrease byproduct production. Maximum activity and yield were achieved using 0.5%Rh-PAA/Al₂O₃-TMPM(0.50), which was chosen for further study of the hydrogenation of 3-substituted aromatic nitro-compounds and determination of the Hammett relationship for this reaction.

3.4 Hydrogenation of Aromatic Nitro-compounds: Hammett Relationship

The 0.5%Rh-PAA/Al₂O₃-TMPM(0.50)catalyst was tested in the hydrogenation reactions of various 3-substituted nitrobenzene derivatives to their corresponding 3-substituted anilines. Due to the distinctive electrochemical and steric structural features of the tested 3-substituted anilines, the results varied as shown in Table 6. In the previous section, we noted that aniline was the only product in the hydrogenation of NBwiththis catalyst. In the

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hydrogenation of substituted 3-nitroarenes bearing -NH₂, -OH, -OCH₃, -CH₃, -Cl, -CN and -NO₂ in the 3-position, the catalyst wasalso 100% selective in generating the corresponding amine product. In all the cases, intermediaries or other product of hydrogenation (-CN, or in any case phenyl ring) or hydrotreatment (-Cl, -OH, -OCH₃ elimination) were not detected. Only in the case of NB-NO₂, 1,3-diamine benzene was detected at higher conversion levels. The higher activity observed for NB hydrogenation also extended to all of the substituted 3-nitrobenzenes, where the following activity sequence was established: NB-NO₂>NB-CN > NB-Cl>NB-NB-CH₃>NB-OCH₃>NB-OH>NB-NH₂. To assess the dependence of rate on the nature of the 3-substituent, we applied the Hammett correlation. The Hammett equation evaluates the effect of a (3- or 4with -NO₂ group as in nitrobenzene) substituent on reaction kinetics and can be used to predict rate and equilibrium constants without prior experimental determination [33, 55, 61]. In this approach, the pseudo-first order constants for the substituted reactants $\left(k_{g,i}\right)$ can be related to that obtained for the non-substituted (or reference) benzene derivative (kg,0) according to:

$$\log\left[\frac{k_{g,i}}{k_{g,0}}\right] = \rho\sigma_i$$

where the ρ term (reaction constant) is an estimation of the charge development during the course of the reaction and provides a measurement of the susceptibility of the system to substituent electronic effects[61, 62]. The σ_i factor is an empirical parameter (values used in this study were taken from Campos *et al.* [55] and Jaffé[61]) that is dependent on the substituent electron donor/acceptor character. This equation was initially conceived for homogeneous systems, where good linear correlations have been established for the

hydrogenation of aromatic nitro-compounds [63]. The involvement of adsorption phenomena, the heterogeneous distribution and nature of active sites, and the highercontribution of steric effects has limited the applicability of the Hammett expression to heterogeneous catalytic systems[61]. Nevertheless, there have been some studies where it has been successfully employed in the liquid-phase hydrogenation treatment of nitroaromatics over solid catalysts[33, 55, 57]. In agreement with a previously reported study of the hydrogenation of 3-nitroarenes [55], at low loadings ($\leq 1.0 \text{ w/w}$ %), noble metals such as Rhshowed higher selectivity for the corresponding 3-substituted anilines, with the exceptionof NB-NO₂. This substrate displayed only -NO₂ group hydrogenation with no detection of intermediates, but only a 40% of conversion of both -NO₂groupsto -NH₂groups was detected.

The fit of the experimental rate data to the Hammett relationship is presented in figure 8. For the NB-OCH₃, NB-OH and NB-NH₂substrates,anon-linear Hammett relation was detected. All other substratesdisplayed linear behavior and generated positive reaction constants (ρ), consistent with a nucleophilic reaction mechanism. The ρ value generated (1.24) indicates a greater dependence of rate on the electronic character of the substituent and is diagnostic of a higher charge development in the reactant \rightarrow intermediate step, which isattributed to electrons flowing towards the aromatic ring in the rate-determining step[33, 55]. The slope of the linear fit gives a positive value for ρ , with chemisorbed H₂ acting as nucleophilic agent that attacks the activated $-NO_2$ group, resulting in the formation of a negatively charged intermediate. This suggests an analogous reaction mechanism for the formation of amines in these heterogeneous catalyst systems.

In the cases of theNB-OCH₃, NB-OH and NB-NH₂ substrates, the corresponding anilines were obtained with the0.5%Rh-PAA/Al₂O₃-TMPM(0.50) catalyst, butdifferent catalytic

performance was observed due to their functional group structures. Low kinetic pseudofirst order constants were found for these three substrates with respect to the general trend(see Table 6). The values calculated show a somewhat linear trend and similar behavior with respect to the other substrates. For example, $k_{(electron-withdrawing groups)} > k_{(NB)} >$ $k_{(electron-donating groups)}$, but the linear relationships did not cross the NB graph (zero point).

We assume that substrates have different electronic contributions from the3-position in the negatively charged intermediate and that this could be one of the explanations for the low conversions we observed. The carboxylate groups on the surface could be forming H-bonding interactions with the substrates. The reaction rates decrease because this H-bondingenhances the inductive donating effect by polarization of the σ -bonds, as shown in scheme 2. The negatively charged intermediate is less stable for these type of substituents in the 3-position. NB-OH and NB-NH₂ can act as H donors or acceptors but NB-OCH₃ can only act as an acceptor. As reported in other Hammett relation studies, NB-OCH₃ in the 3-position displays electron-with drawing character with respect to the other substituents in the aromatic ring[62, 64], but in our case this substrate displays an electron-donating effect because k_{NB} > k_{NB-OCH3}.

All of these results are indicative of a partially charged transition state with a ρ value comparable to those reported for liquid-phase heterogeneous hydrogenations (Ir/ZrO₂, 0.639 [55], β -Mo₂N 0.4 [33]and Pt/SiO₂-AlPO₄ 0.1–2.0 [57]). The pseudo-first order constant displacement detected for NB-OCH₃, NB-OH and NB-NH₂suggests a common reaction mechanism for the formation of amines inthese heterogeneous catalyst systems.

4. CONCLUSIONS

A novel polymer-inorganic hybrid material, PAA/Al₂O₃-TMPM, was prepared usingin situ radical polymerization and a sol-gel process with acrylic acid and organometallic oxide precursors. These new solid-based composites are a SIHN and changes its properties when different TMPM/(TMPM+TSBAI)molar ratios are used. IncreasingTMPM in the composite results in an increase in thermal stability and a decrease in surface area. The Rh catalyst was synthesized by an ionic exchange process and in situ H2 reduction (to 398 K) using RhCl₃as the inorganic precursor to produce catalysts with a mixture of Rh nanoparticles and Rh(µ-O₂CR)_x complexes (where x: 2 or 4). The catalystsused at 1 wt %, exhibited different residual $Rh(\mu-O_2CR)_x$ contents that decreased with increasing TMPM in the support. All of the prepared systems were tested as catalysts in the liquid-phase hydrogenation of NB and were 100% selective with respect to -NO₂ group reduction. The most active and selective catalyst was 0.5%Rh-PAA/Al₂O₃-TMPM(0.50), which was used as anoptimum catalyst for the hydrogenation of a range of 3-substituted (-H, -OH, -OCH₃, -CH₃, -Cl, -CN, and -NO₂) nitrobenzenes. The reaction proceeds via a nucleophilic mechanism where the presence of electron-withdrawing ring substituents served to increase the rate, as demonstrated by the linear Hammett relationship and positive reaction constant $(\rho = 1.24)$. The obtained results demonstrate the potential of polymer hybrid compositesupported nanoparticles to promote the clean production of amino-compounds by catalytic nitrobenzene reduction.

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Legend of theSchemes

Scheme 1. Reaction pathways of the hydrogenation of aromatic nitro-compounds hydrogenation proposed by Kratky et al [56].

Scheme 2. Schematic H bond interaction on 0.5% Rh-PAA/Al₂O₃-TMPM(0.50) catalyst.

Legend of the Figures

Figure 1.FT-IR spectra of PAA/Al₂O₃-TMPM(x) composites. Solid line, x: 0; dash line, x: 0.125; dot line x: 0.25; short dash dot line, x: 0.50.

Figure 2. Thermogravimetric analysis for PAA/Al₂O₃-TMPM(x) composites.(a) TGA and (b) DTGA. Solid line, x: 0; dash line, x: 0.125; dot line x: 0.25; short dash dot line, x: 0.50.

Figure 3. Scanning electron microscopy (SEM) photographs of PAA/TMPM(x)/Al₂O₃ composites. (a) x: 0; (b) x: 0.125; (c) x: 0.25; (d) x: 0. 50.

Figure 4. The powder XRD patterns of 0.5% Rh-PAA/Al₂O₃-TMPM(x) catalysts. (a) x: 0; (b) x: 0.125; (c) x: 0.25; (d) x: 0.50.

Figure 5. Representative TEM Micrograph and Rh nanoparticle size distribution measurements for 0.5%wt Rh-PAA/Al₂O₃-TMPM(x) catalysts.(a) x: 0; (b) x: 0.125; (c) x: 0.25 and (d) x: 0.50.

Figure 6. Solid-state CPMASNMR of 0.5% Rh-PAA/Al₂O₃-TMPM(x) catalysts. (A) 13 C and (B) 29 Si.

Figure 7. Activity curves based on NB conversion for all the synthesized catalysts. Reaction conditions: NB concentration: 0.02 molL^{-1} , catalyst mass: 0.100 g, P_{H2} : 20 bar, mixing speed: 800 rpm, solvent: absolute ethanol.

Figure 8. Hammett plot for the selective 3-subtiuted aromatic nitro-compounds hydrogenation. Reaction conditions: substrate concentration: 0.02 molL^{-1} , catalyst mass: 0.100 g, P_{H2}: 20 bar, mixing speed: 800 rpm, solvent: absolute ethanol.





Nominal			Mass loss (%)		
TMPM/(TMPM+TSBAI)	$T_W^*(K)$	T _d (K)	First	Second	
Mole ratio			Tinst	Second	
0	377	730	4.8	47.8	
0.125	346	649	2.3	46.3	
0.25	345	639	2.4	51.7	
0.50	340	621	2.6	55.6	

*Temperature of water desorption.

Table 2

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Table 2. EDS data of PAA/Al_2O_3 -TMPM(x) composites. In brackets the atomic percent by EDS analysis.

PAA	Nominal (wt%)				Surface (wt%)				
AI_2O_3 -1 MPM(X)	С	Al	Si	S	С	0	Al	Si	S
0	25.12	8.96	-	4.46	64.09 (71.32)	32.35 (27.03)	2.99 (1.48)	-	0.33 (0.14)
0.125	27.58	6.74	2.00	3.83	64.35 (71.58	32.45 (27.35)	1.74 (0.99)	0.51 (0.28)	0.25 (0.11)
0.25	29.43	5.06	3.51	3.36	64.65 (71.45)	32.21 (27.41)	1.47 (0.73)	0.87 (0.47)	0.22 (0.09)
0.50	32.04	2.71	5.63	2.70	64.79 (71.64)	32.82 (27.24)	1.14 (0.56)	1.94 (1.05)	0.17 (0.07)

Table 3. Physicochemical properties of the catalysts: elemental analysis by ICP-MS, S_{BET} , pore volume, pore diameter, metallicnanoparticles size diameter and dispersion of 0.5wt% Rh-PAA/Al₂O₃-TMPM(x) catalysts.

0.5wt%Rh-	Rh (%wt)	S _{BET}	Pore Volume	Diameter Pore	d _{TEM}	D _{TEM}
PAA/Al ₂ O ₃ -		(m^2g^{-1})	(cm ³ STP g ⁻¹)	(nm)	(nm)	
TMPM(x)						
0	0.49	140	0.37	100	4.6	0.23
0.125	0.49	50	0.09	87	4.3	0.25
0.25	0.45	35	0.08	87	4.1	0.27
0.50	0.48	25	0.06	86	4.1	0.27

PC -

Table 4

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0.5%Rh-PAA/ Al ₂ O ₃ -TMPM(x)	Al2p (eV)	C1s (eV)	O1s (eV)	Rh3d _{5/2} (eV)	Si2p (eV)	Rh/Alat	Si/Alat	C ₂₈₈ /C ₂₈₆
0	74.5	284.8 (58) 286.8 (20) 288.4 (22)	531.7	308.4 (34) 310.2 (66)	-	0.047	-	1.152
0.125	74.6	284.8 (67) 286.9 (15) 288.5 (18)	531.7	308.3 (38) 310.2 (62)	-	0.024	-	1.130
0.25	74.6	284.8 (60) 286.7 (20) 288.7 (20)	531.7	308.5 (52) 310.3 (48)	101.5	0.033	0.167	1.000
0.50	74.6	284.8 (62) 286.8 (19) 288.4 (19)	531.7	308.2 (60) 310.0 (40)	101.3	0.073	0.324	1.000

Table 4. Binding energies (eV) of internal electrons and atomic surface ratio of 0.5wt%Rh-PAA/Al₂O₃-TMPM(x) catalysts.

Table 5.Kineticdata for NB hydrogenation on 0.5wt%Rh-PAA/Al₂O₃-TMPM(x) catalysts. Reaction conditions: NB concentration: 0.02 molL^{-1} , catalyst mass: 0.100g; stirring speed: 800 rpm and solvent: absolute ethanol.

0.5%Rh-PAA/	X ^a	Yield ^b , An	k _g	TOF ^c
Al ₂ O ₃ -TMPM(x)	(±1%)	(±1%)	(h ⁻¹ g ⁻¹)	(h ⁻¹)
0	67.5	98.2	1.53	183
0.125	73.5	99.1	1.95	200
0.25	88.0	99.7	2.86	241
0.50	97.4	100	3.46	259

^a Conversion (X) at 480 minutes of reaction

^bYield_{An}, defined as (100 \cdot mol An/(mol An + mol intermediaries)). Intermediaries:

nitrosobenzene and/orphenylhydroxylamineat 240 minutes of reaction.

^cTurnover frequencies, defined as the 4 hour catalytic activity

Table 6. Kinetic data and σ parameterfor 3-subtituited aromatic nitro-compounds hydrogenation on 0.5wt%Rh-PAA/Al₂O₃-TMPM(0.50) catalyst. Reaction conditions: substrate concentration: 0.02 molL⁻¹, catalyst mass: 0.100g; stirring speed: 800 rpm and solvent: absolute ethanol.

	X ^a	Selectivity ^b , An	kg	σ ^c
Substrate	(± 0.2%)	(± 0.2%)	(h ⁻¹ g ⁻¹)	
NB-NH ₂	11.0	100	0.18	-0.161
NB-CH ₃	83.3	100	1.65	-0.069
NB-OH	33.2	100	0.64	-0.002
NB-OCH ₃	65.2	100	1.47	0.115
NB-Cl	98.9	100	7.83	0.373
NB-CN	96.2	100	10.31	0.678
NB-NO ₂ ^d	100	87.1	12.88	0.710

^aConversion (X) at 480 minutes of reaction.

^bYield_{An}, defined as (100 \cdot mol An/(mol An + mol intermediaries)). Intermediaries: 3-

subtituited: nitrosobenzene and/or phenylhydroxylamine.

^cData from [61]

^ddiaminobenzene as the over-hydrogenation product at 3 h of reaction.



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(B)

0.5Rh%-PAA/Al2O3-TMPM(0.0)

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