The purpose of this study was to evaluate on the catalytic activity nanostructured systems of ruthenium and rhodium stabilized in ionic liquids derived from imidazole: IL=butylmethylimidazolide tetrafluoroborate [BMIM][BF₄] and IL=butylmethylimidazolide hexafluorophosphate [BMIM][PF₆] in the biphasic hydrogenation of eugenol under mild reaction conditions T=80°C, P=100psi during 4 hours. The metallic nanoparticles (NPs-M) were synthesized using the ligand hydrogenation displacement reaction for the ruthenium III tris(acetylacetonate), [Ru(acac)₃], and bis-μ-chloro-di(1,5-cyclooctadieno) dirhodium(I), [Rh(COD)Cl]₂, showing a mean particle size between (2.0±0.2) nm and (4.0±0.2) nm. The nonstructured systems Rh/IL, Ru/IL, and Ru/IL show similar activities and different from the Rh/IL system. On the other hand, the systems stabilized in the IL are more selective towards the formation of the 2-methoxy-4-phenylphenol than the systems stabilized in the IL. Nevertheless, in general, the catalysts were good for hydrogenating eugenol, resulting in Rh/IL, nanoparticles less reactive than Rh/IL, Ru/IL, and Ru/IL.

Keywords: Nanoparticles, ionic liquids, biphasic hydrogenation, eugenol.

1. INTRODUCTION

Eugenol is part of the family of allylbenzenes, which in turn are part of the natural olefins readily available from biomass, forming alternative materials from renewable sources. Eugenol is a phenolic derivative commonly known as clove essence, which has been used for several centuries in dental practice, due to its pharmacological properties, since it has many uses; the oldest dental cement is a mixture zinc-oxide-eugenol which has sedative and palliative property of pulpal pain, likewise the oil is used for spongy bleeding gums and gingivitis. Within the many reported properties of eugenol are: neuroprotection, inhibition of the biosynthesis of thromboxane, anti-inflammatory, anticancer, anti- ischemic, antihistamine and antianaphylactic. The cosmetic industry uses eugenol in soaps, perfumes, and shampoo production. In the food industry it is used to give aromas to prepared foods, alcoholic drinks, and soft drinks, among others. It is also used as a starting material to produce other compounds with higher aggregated value, such as 2-methoxy-4-propylphenol. This compound was used as a raw material in the synthesis of 1,2-dimethoxy-4-propylbenzene, the pheromone of the male fruit fly (Dacus dorsalis Hendel) used in control of pests traps in many crops being 50% more effective than methyl eugenol which was initially used by the farming community.

The specialized literature reports the hydrogenation of eugenol and isoeugenol using Pt, Pd and Ni supported in X or Y zeolites. The authors reported that the increase in acid hydrothermal treatment displacement for the ruthenium III tris(acetylacetonate), [Ru(acac)₃], and bis-μ-chloro-di(1,5-cyclooctadieno) dirhodium(I), [Rh(COD)Cl]₂, showing a mean particle size between (2.0±0.2) nm and (4.0±0.2) nm. The nonstructured systems Rh/IL, Ru/IL, and Ru/IL show similar activities and different from the Rh/IL system. On the other hand, the systems stabilized in the IL are more selective towards the formation of the 2-methoxy-4-phenylphenol than the systems stabilized in the IL. Nevertheless, in general, the catalysts were good for hydrogenating eugenol, resulting in Rh/IL, nanoparticles less reactive than Rh/IL, Ru/IL, and Ru/IL.

Keywords: Nanoparticles, ionic liquids, biphasic hydrogenation, eugenol.

The purpose of the present work is to study biphasic catalytic activity of rhodium and ruthenium nanoparticles, stabilized in ionic liquid, in the eugenol hydrogenation reactions, under mild reaction conditions.

2. EXPERIMENTAL

2.1 Materials

The eugenol (4-allyl-2-methoxyphenol) used as substrate for the biphasic hydrogenation was Sigma Aldrich technical grade 99% purity. The n-hexane used as solvent was 99% purity analysis from Merck. The evaluated ionic liquids synthesized using the ligand were synthesized using the ligand hydrogenation displacement reaction for the ruthenium III tris(acetylacetonate), [Ru(acac)₃], and bis-μ-chloro-di(1,5-cyclooctadieno) dirhodium(I), [Rh(COD)Cl]₂, showing a mean particle size between (2.0±0.2) nm and (4.0±0.2) nm. The nonstructured systems Rh/IL, Ru/IL, and Ru/IL show similar activities and different from the Rh/IL system. On the other hand, the systems stabilized in the IL are more selective towards the formation of the 2-methoxy-4-phenylphenol than the systems stabilized in the IL. Nevertheless, in general, the catalysts were good for hydrogenating eugenol, resulting in Rh/IL, nanoparticles less reactive than Rh/IL, Ru/IL, and Ru/IL.

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Keywords: Nanoparticles, ionic liquids, biphasic hydrogenation, eugenol.
The nanoparticles characterization was carried out by a transmission electron microscopy (TEM), in an electronic transmission electron microscope FEI Type: Tecnai G² Spirit BioTwin, Model: 9432 050 18411.

All the reactions were carried out under an inert argon (Ar) atmosphere using schlenk-type techniques for the handling of air-sensitive compounds. As for the solvents used tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), diethyl ether and n-hexane, all were dried by the traditional methods.

2.3. Synthesis of de ionic liquids

The synthesis of the ionic liquids was performed in two stages: (a) the cation formation followed the methodology proposed by Dupont et al 15 allowing the

| Ionic liquids (ILs)          | FTIR Spectral bands                      | ¹H-NMR 6 (ppm)                               |
|-----------------------------|------------------------------------------|----------------------------------------------|
| IL₁ = [BMIM][BF₄]          | 3160 [y(C-H) aromatics], 2965 [y(C-H) aliphatic], 1570 y 1467 [y(C=C)], 1061 U(BF) | 8.70 [s, 1H, H(2)]; 7.47[s, 1H, H(4)]; 7.37 [s, 1H, H(4)]; 7.15 [s, 1H, H(5)]; 4.09 [2H, 1H(C₆)]; 3.85 [s, 3H, H(10)]; 1.72 y 1.20 [2 m, 4 H, H(7) y H(8)]; 0.83 [t, 3 H, 1H₄=5.31, H(9)] |
| IL₂ = [BMIM][PF₆]          | 3177 y 3100 [U(C-H) aromatics], 2956,2936 y 2880 [U(C-H) Alifáticos], 1576 y 1466 [U(C=C)], 857 U(PF) | 8.66 [br s, 1H, H(2)]; 7.47[br s, 2H, H(4) y H(5)]; 7.37 [br s, H(6)]; 4.19[br s,3H, H(10)]; 1.34 [br s, H(9)]. |

The results reported in Table 1 reflect bands and signals that, when compared with that reported in the literature 17, 18, corroborate the obtaining of the desired ionic liquids.

2.4. Synthesis of rhodium nanoparticles

The synthesis of the nanosystems were carried out using the ligand hydrogenation displacement reaction of the organometallic [RhCODCl]₂ precursor in the presence of the respective IL dissolved in THF as proposed by Domínguez et al 15. The precursor was dissolved in THF and the corresponding IL in THF was added, at room temperature, in a 1Rh:4IL ratio. This mixture was transferred to the Parr reactor, charged with 100psi H₂ pressure, and left under constant stirring at 60°C. After 24 hours the reaction was stopped, a dark suspension of stabilized rhodium nanoparticles was obtained. The solvent was decanted via cannula and the remaining solid was washed thoroughly with dry THF in order to eliminate reaction by products and excess reactants. The rhodium nanosystems synthesized were dried under vacuum and stored under argon until later use. The nanosystems obtained will be named Rh/IL₁ and Rh/IL₂.

2.5. Synthesis of ruthenium nanoparticles

The synthesis of the ruthenium nanoparticles was carried out using Scholten et al 20 reported method which implies the ligand hydrogenation displacement reaction of a salt or organometallic complex. In this case [Ru (acac)₃] and an ionic liquid as a stabilizing agent (IL₁ and IL₂) with a molar ratio 1Ru: 7LI were previously dissolved in dry THF at room temperature, under an inert Ar atmosphere. Finally, the Parr reactor was charged with the mixture, with 58 psi of hydrogen (H₂) and left under constant agitation for 48 hours at 75°C, after which the reactor was discharged, obtaining a dark suspension and fine black particles.

2.6. Biphasic hydrogenation of eugenol

Biphasic eugenol hydrogenations were performed using the nanostructured rhodium and ruthenium catalysts: Rh/ IL₁, Rh/ IL₂, Ru/ IL₁, and Ru/ IL₂. The methodology carried out by Melean et al 14 was modified, such that the substrate was reacted with hydrogen in the presence of the nanostructured system stabilized with ionic liquid, an organic solvent was used to ensure the separation of the reaction products and the catalytic phase. In this sense, a Parr reactor was charged under inert atmosphere, with 6 mmol of eugenol, 3 ml of n-hexane, 0.5 ml of ionic liquid (IL₁ and IL₂) and 5 mg of each of the Ru catalysts (nanoparticles), of Ru/ IL₁ and Ru/ IL₂ and Rh (nanoparticles of Rh/ IL₁, and Rh/ IL₂) with 100 psi of H₂ at a temperature of 80°C. The catalytic evaluations were carried out between 0.5 and 8 hours. At the end of the reaction time, the phases were separated for analysis by gas chromatography and mass spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Characterization of rhodium and ruthenium nanoparticles by TEM

The bright field analysis by TEM for the nanostructured metal systems, stabilized in ionic liquids (M₂IL₄), confirmed that all the synthesized catalysts are made of nanometric particles. However, the micrographs did not yield a clear visualization of the interparticle planes, therefore, the indexation of the nanostructures could not be determined. Rh/ IL₁ nanoparticle micrograph in Figure 1 (a) shows strong agglomeration of the particles, particles clusters, clusters of large particles overlapping the small particles, and few structures with hexagonal faceted particle definition are also appreciated. However, when viewing Figure 1 (b) corresponding to electron diffraction of the material, the presence of rings is observed, which allows us to infer the existence of very small nanoparticles in the material 21, the bright dots present in the rings indicate the presence of a few faceted structures which diffract in the same direction. 21 Given that the dispersion of the size of the nanoparticles is less than 12%, it could be established that the material is homogeneous as established in the specialized literature.

![Figure 1](image)
Figure 2 shows the histogram of particle size distribution for the nanostructured system of Rh/IL1 with a mean size distribution of (2.6±0.2) nm.

![Figure 2. Particle size distribution histogram for Rh/IL1 with a mean particle size of (2.6±0.2) nm.](image)

Figure 3 shows (a) bright field TEM analysis of the Rh/IL2 nanoparticles, a large agglomeration can be observed, particle clusters, clusters of large particles overlapping small particles, some structures with hexagonal particle definition and appearance of ionic liquid encapsulating the particles. In Figure 3 (b) the electrons diffraction is very similar to that of Rh/IL1 system although the presence of fewer and very diffuse bright dots in the diffraction rings, leads to infer that the faceted particles are scarcer than in the Rh/IL1 system. Once again this analysis allows the establishment of the nanomaterial size homogeneity.

![Figure 3. Images corresponding to micrographs of Rh/IL2 nanoparticles by transmission electron microscopy (TEM) (a) clear field and (b) electron diffraction.](image)

Through the particle size distribution histogram of this system (Figure 4), we determined that the nanoparticles have an average size of (4.0±0.2) nm, unlike the size distribution obtained for the Rh/IL2 in this case the distribution is bimodal, maintaining the nanometric scale. In this sense, when compared with what is reported in the literature for the synthesis of rhodium nanoparticles, particle sizes vary from 2 nm, while other investigations in which rhodium nanoparticles stabilized in ionic liquids were synthesized from the organometallic complex [Rh(μ-Cl)(COD)]2, 2.13 - 6.4 nm nanoparticles were obtained. Thus, the nanoparticles obtained in this investigation are within the reported size.

![Figure 4. Rh/IL2 Histogram of nanoparticles with particle size distribution of (4.0±0.2) nm.](image)

The bright field TEM analysis for Ru/IL1 system shown in Figure 5 (a) reveals spherical and oval shape nanoparticles, strong agglomeration of this system and less ordered crystallinity. While in the electron diffraction visualized in Figure 5 (b), the presence of well-defined diffraction rings with bright dots is observed, which allows inferring the coexistence of very small nanoparticles and larger particles that were not possible to measure in the light field micrographs. Therefore, the amount of bright dots found in the rings shows that there is percentage of particles that are faceted; consequently they diffract in particular angles, which show heterogeneity in the material.

![Figure 5. Images corresponding to micrographs of Ru/IL1 nanoparticles by transmission electron microscopy (TEM) (a) clear field and (b) electron diffraction.](image)

The particle size distribution histogram in Figure 6 for the nanostructured system of Ru/IL1 is shows an average particle size of (2.0±0.2) nm, defining it as a nanomaterial.

![Figure 6. Histogram of Ru/IL1 nanoparticles: particle size distribution (2.0±0.2) nm](image)

In Figure 7 (a) the bright field TEM micrograph of Ru/IL2 strong agglomeration is observed with small particle clusters evenly distributed. Although for this material the mean distribution size of (2.1±0.1) nm is very similar to that found Ru/IL1, its worth noting the lack of bright dots in the electron diffraction image (b). This leads us to infer that this material is composed only of small nanoparticles.

![Figure 7. Images corresponding to micrographs of Ru/IL2 nanoparticles by transmission electron microscopy (TEM) (a) clear field and (b) electron diffraction.](image)
The histogram of particle size distribution for Ru/IL$_2$ nanoparticles is shown in Figure 8, once again confirming the nanometric character of the catalyst.

**Figure 8.** Histogram of Ru/IL$_2$ nanoparticles: particle size distribution (2.1±0.1) nm

Comparing the ruthenium nanosystems synthesized here (Ru/IL$_1$ and Ru/IL$_2$) with those reported in the literature where Ru (0)-NPs nanoparticles were obtained from [Ru (COD) (2-methylalyl)$_2$] in IL= nHM$_2$N$_2$Tf$_2$ with average size of (2.0 ± 0.3) nm$^{23}$; and Ru (0) -MPs nanoparticles made in other ionic liquids where the average size is in the range of (2-3) nm$^{24}$, it is confirmed that the synthesis method starting from the [Ru(acac)$_3$] precursor was effective in obtaining nanoparticles with similar sizes.

### 3.2. Biphasic hydrogenation of eugenol

Once the catalytic tests corresponding to the biphasic hydrogenation of eugenol were carried out, the gas chromatography/mass chromatography (GC/MS) and gas chromatography (GC) analysis corroborated the presence of the substrate (eugenol) and three products. In literature these correspond to: (1) eugenol, (2) 2-methoxy-4-propylphenol, (3) cis-isoeugenol and (4) trans-isoeugenol. The resulting 2-methoxy-4-propylphenol (2) is the main hydrogenation product. The reaction scheme in Figure 9 displays the aforementioned products that were confirmed by chromatography and agree with that reported by Kadarohman$^{25}$.

**Figure 9.** Reaction scheme for the biphasic hydrogenation catalysis of eugenol ref$^{13}$.

In the present work we studied the catalytic activity of each nanostructured system Rh/IL$_1$, Rh/IL$_2$, Ru/IL$_1$ y Ru/IL$_2$ after 0.5; 1; 2; 3; 4 and 8 hours reaction time. In Figure 10 we can appreciate the biphasic hydrogenation profile of each catalyst studied. Rh/IL$_2$, Ru/IL$_1$ and Ru/IL$_2$ have the same behavior, whereas Rh/IL$_1$ have an appreciably lower catalytic activity. Ru/IL$_1$ and Ru/IL$_2$ systems reach maximum conversion, above 97%, after four hours; Rh/IL$_1$ achieves 81% conversion in the same time without reaching its plateau; whereas for Rh/IL$_1$ only reaches 53% conversion, and even after 8 hours reaction it only achieves 60% conversion. These results show that the ruthenium nanosystems here studied are more active than the rhodium counterparts for the biphasic catalytic hydrogenation of eugenol. Nevertheless, the literature reports the hydrogenation reaction of myrcene to be less active with ruthenium organometallic complexes than rhodium complexes$^{26}$. The difference in activity between the two metals could well be ascribed to the nanometric characteristics of the materials here studied.

**Figure 10.** Biphasic hydrogenation of eugenol with nanoparticles of: Rh/IL$_1$, Rh/IL$_2$, Ru/IL$_1$ y Ru/IL$_2$.

In the study of the selectivity of the catalytic systems towards 2-methoxy-4-propylphenol (Table 2) the Ru/IL$_1$ y Rh/IL$_1$ systems show selectivities very near 100%, during all reaction times; whereas those catalysts stabilized in IL$_2$ showed varied selectivities above 84%. Then again, the observed change in the formation of products can be attributed to the intrinsic characteristics of the nanostructured catalyst.
Table 2. Conversion and selectivity for the hydrogenation of eugenol using Rh/IL₁, Rh/IL₂, Ru/IL₁, and Ru/IL₂ nanoparticles.

| Nanoparticles | Time (h) | Conversion (%) | Selectivity[4] (% | Selectivity[1] (% | Selectivity[2] (% | Selectivity[3] (%) |
|---------------|---------|---------------|----------------|----------------|----------------|----------------|
| Rh/IL₁        | 0.5     | 25            | 100            | —              | —              | —              |
|               | 1       | 36            | 100            | —              | —              | —              |
| Rh/IL₂        | 2       | 43            | 100            | —              | —              | —              |
| Ru/IL₁        | 3       | 50            | 100            | —              | —              | —              |
| Ru/IL₂        | 4       | 53            | 97             | 1              | 2              | —              |
|               | 8       | 60            | 100            | —              | —              | —              |
|               | 0.5     | 22            | 100            | —              | —              | —              |
|               | 1       | 38            | 84             | 9              | 7              | —              |

Table 3. Conversions, activities and particle size for the biphasic hydrogenation of eugenol using rhodium and ruthenium nanoparticles stabilized in IL₁ and IL₂.

| Catalyst | Particle size (nm) | Conversion (%) | Selectivity[2] (%) | TOF h⁻¹ |
|----------|--------------------|----------------|-------------------|---------|
| Rh/IL₁   | 2.6±0.2            | 53             | 97                | 1596    |
| Rh/IL₂   | 4.0±0.2            | 81             | 94                | 2440    |
| Ru/IL₁   | 2.0±0.2            | 99             | 99                | 2982    |
| Ru/IL₂   | 2.1±0.1            | 97             | 99                | 2922    |

Conditions: Rh/IL₁, Rh/IL₂, Ru/IL₁ and Ru/IL₂ = 0.005 g, n-hexane = 3 ml, IL₁ = [BMIM][BF₄] and IL₂ = [BMIM][PF₆] = 0.5 ml, substrate (eugenol) = 1 gr, T = 80 °C, P = 100 psi, t = 4 h. [a] Selectivity= 2-methoxy-4-propylen. (3) cis-isoeugenol and (4) trans-isoeugenol.

3.3. Mercury drop test

In order to test the absence of metallic particles in the reaction mixture, the biphasic hydrogenation of the eugenol was tested by adding a drop of liquid mercury to the reaction mixture. The results obtained: (a) under the established study conditions for the Ru/IL₁ = 0.005 g, n-hexane = 3 ml, IL₁ = [BMIM][BF₄] and IL₂ = [BMIM][PF₆] = 0.5 ml, substrate (eugenol) = 1 gr, T = 80 °C, P = 100 psi, t = 4 h, yielded 99% conversion and 99% selectivity towards the formation of 2-methoxy-4-propylphenol; (b) adding a drop of mercury to the reaction mixture under the conditions mentioned above did not generate any products, and 100% of the substrate (eugenol) was recovered. This indicates that probably the active metal nanoparticles stabilized in the ionic liquids formed an amalgam with mercury inhibiting biphasic catalysis, thus corroborating that metallic nanoparticles are responsible for the conversions and selectivities towards 2-methoxy-4-propylenol.

CONCLUSIONS

By the method of reduction and ligand displacement ruthenium and rhodium nanoparticles stabilized in ionic liquids nanoscale ILs corresponding to that reported in the literature were synthesized. The synthesized nanometric systems were active for the hydrogenation of eugenol biphasic under mild reaction conditions. There are no reports in the literature of biphasic catalysis with nanometric systems of these metals for the hydrogenation of eugenol. Ruthenium nanosystems in this study were more active than the rhodium counterparts for the biphasic catalytic hydrogenation of eugenol, under the mild conditions used. Both metals stabilized in the ionic liquids, under the mild conditions described herein, are highly selective towards the product 2-methoxy-4-propylenol.

ACKNOWLEDGMENTS

The authors wish to thank the Laboratory of Organometallic Synthesis (SOM) of the School of Chemistry, Faculty of Sciences of the Central University of Venezuela for its material contribution and support in the synthesis of nanoparticles; also to the Chemical Research Center (CIQ) of the Faculty of Engineering of the University of Carabobo (UC) for allowing the development of research and to the Microscopy Laboratory of the Chemical Center, Venezuelan Institute of Scientific Research (IVIC).
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