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INSIGHTS FROM DIFFERENTIAL SCANNING CALORIMETRY AND CYCLIC VOLTAMMETRY ANALYSES: STUDIES OF THE SYNERGISTIC EFFECT OF TWO DIFFERENT METALLOCENES ON THE MAIN OXIDIZING AGENT FOR SOLID ROCKET MOTOR

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ABSTRACT

To understand the synergistic catalytic effect on the thermal degradation of Ammonium Perchlorate (AP) when the metal fragments are in the same molecule or not, we compared three reported compounds: [(Cp*)$_2$Ni] (**1**), [(Cp*)$_2$Ru] (**2**), and [Cp*Ni-s-Ic'-RuCp*] (**3**), as potential burning rate catalysts. We conducted a differential scanning calorimetry (DSC) analysis of compound (**3**), which showed an increase in the high-temperature decomposition (HTD) of AP to 418 ºC and a decrease in the energy release to 938 $J\cdot g^{-1}$. These results were compared to those of the different metallocenes, namely (**1**) (HTD: 434 ºC and 1300 $J\cdot g^{-1}$), (**2**) (HTD: 361 ºC and 1828 $J\cdot g^{-1}$), and the mixture of (**1+2**) (HTD: 354 ºC and 2054 $J\cdot g^{-1}$). Our results suggest that the mixture of metallocenes is a suitable and competitive alternative to be used as an enhancer of solid composite propellants. In addition, cyclic voltammetry is used to investigate the electrochemical processes of compounds (**1**), (**2**), and (**3**). The electrochemically active species exhibit noteworthy oxidation peaks, revealing electronic communication between the three different compounds in the cases of (**1**), (**2**), and (**3**), as evidenced by the results obtained from the analysis.

Keywords: Thermal decomposition; Burning Rate Catalysis; Composite Solid Propellant; cyclic voltammetry.

1. INTRODUCTION

Rocket technology research is currently attracting significant attention due to its potential applications, especially in the aerospace industry. This is a crucial step towards expanding human exploration into space. Investigating the burn rate (BR) catalyst and its impact on the thermal degradation of the primary oxidizing agent for solid rocket motors, ammonium perchlorate (AP), is essential for improving the thrust and acceleration associated with the hot gases inside the combustion chamber. This increased thrust and acceleration produce enough pressure to force the gases out of the exhaust port (nozzle), and the kinetic energy generated by this motion produces the propulsion [1].

Nowadays, different types of BR catalysts have been studied, where they have mainly been related to iron derivatives such as nanoparticles [2-3], coordination complexes,[3] and ferrocene derivatives [5-7]. Regarding ferrocene derivatives have excellent properties and compatibility with the commonly used binder agent, HTPB/AP (hydroxyl-terminated polybutadiene); these specific properties generate a stable composite solid propellant [8-9].

The effect of BR catalyst candidates on the combustion behavior of composite solid propellants is typically measured by their impact on the thermal degradation of AP. Adequate BR catalysts have been shown to cause a shift to the left in the high-temperature decomposition (HTD) peak of AP, accelerating its decomposition and increasing its released heat [10-12]. However, unlike ferrocene derivatives, dissimilar BR catalysts have not been extensively explored, except for our group's work employing heterobimetallic compounds [7] and bimetallic ruthenocenes compounds to catalyze the thermal decomposition of AP[13-14]. These ruthenium complexes have demonstrated a catalytic effect on the HTD peak of AP.

On the other hand, to improve the thermal catalytic effect, studies have been carried out on the synergistic effect of two different metals in relation to nanoparticles [9]. Liu and coworkers investigated the effect of different metal nanoparticles. The addition of Cu and Ni NPs (5 wt%) lowered the HTD peak of AP, but the use of mixed metal nanoparticles produces a synergistic effect in the catalytic activity than single-phase metals. To the extent of our knowledge, the mixture of metallocene-type complexes as BR catalysts has not been explored yet.

For the reasons stated above, in this article we study the previously synthesized heterobimetallic complex [Cp*Ni-*s*-Ic'-RuCp*] compared with the monometallic fragments bis(pentamethylcyclopentadienyl)nickel [(Cp*)$_2$Ni] and bis(pentamethylcyclopentadienyl) ruthenium [(Cp*)$_2$Ru], to understand the cooperative effect when the metal moiety is in the same molecule or not and what will be their effect on the thermal decomposition of AP.

Furthermore, cyclic voltammetry was used to investigate the oxidation processes of these complexes and to compare the heterobimetallic [Cp*Ni-*s*-Ic'-RuCp*] complex with the monometallic complexes [(Cp*)$_2$Ni] and [(Cp*)$_2$Ru].

2. EXPERIMENTAL SECTION

2.1. General Information of the compounds

Unless specified otherwise, all manipulations were carried out within a dry box equipped with a Dry-Train cleaner Model HE493 and a vacuum line with a diffusion mercury pump, using Schlenk-tube techniques under an inert atmosphere of dry nitrogen or argon. Anhydrous solvents were distilled and dried under a nitrogen atmosphere from Na/benzophenone for tetrahydrofuran (previously distilled from $AlLiH_4$), toluene, and hexane, and freshly distilled from P_2O_5 in the case of CH_2Cl_2 [16].

The DSC analysis was conducted using a Perkin Elmer DSC 4000 instrument with a heating rate of 5 °C min^{-1} under nitrogen atmosphere, ranging from 140 to 445 °C. The aim was to evaluate the catalytic performance of the monometallic and heterobimetallic compounds on the thermal decomposition of AP. For this purpose, a physically mixed and ground mixture of the organometallic complexes and AP in a specific weight ratio (3 and 5 wt.% average sample mass = 5.430 mg) was prepared for the DSC analysis.

An airtight three-electrode cell, connected to an argon line, was employed to carry out cyclic voltammetry experiments. The working electrode was a platinum disc, approximately 3 mm in diameter, while the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum wire. A BAS CV-50 Voltammetric Analyzer Potentiometer, powered by a Pentium II 350 MHz processor, was used to record the currents and potentials. For each electrochemical experiment, the first fraction of distilled CH_2Cl_2 was utilized. This fraction was collected over phosphorus pentoxide and heated at reflux once again. Prior to use, the supporting electrolyte, $[NBu_4]BF_4$, was dried under vacuum and heated at 60°C for 3 hours. The synthesis procedure of the following complexes has been reported previously, [(Cp*)$_2$Ni] (**1**), [10] [(Cp*)$_2$Ru] (**2**),[11] and [Cp*Ni-*s*-Ic'-RuCp*] (**3**). [12]

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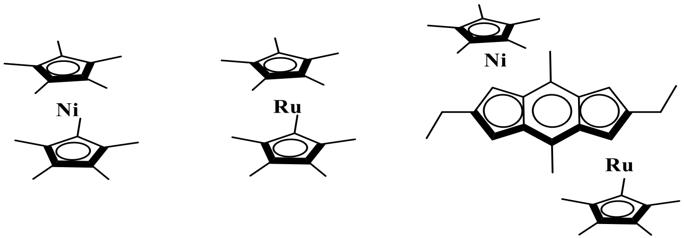
3. RESULTS AND DISCUSSION

Since homo- and heterobimetallic complexes have been reported to be efficient catalysts for the thermal decomposition of AP [6,13,14], particularly derivatives of ruthenocenes, this motivated us to test the activity of heterobimetallic complex [Cp*Ni-*s*-Ic'-RuCp*] (**3**), as burning rate catalysts in comparison with the bis(pentamethylcyclopentadienyl)nickel (**1**), bis(cyclopentadienyl)ruthenium (**2**), in order to observe some cooperative effect when the similar fragments are in the same molecule or not. Figure 1 shows the chemical structure of the catalysts used in this work.



(1) **(2)** **(3)**

Figure 1: Bis(pentamethylcyclopentadienyl)nickel [(Cp*)$_2$Ni] (**1**), Bis(pentamethylcyclopentadienyl) ruthenium [(Cp*)$_2$Ru] (**2**), and heterobimetallic complex Cp*Ru(2,6-diethyl-4,8-dimethyl-sindacene)NiCp* [Cp*Ni-*s*-Ic'-RuCp*] (**3**) compared in this work.

Cyclic Voltammetry Studies

For comparison purposes, cyclic voltammetry measurements were conducted in 10 ml of CH_2Cl_2 with a concentration of 0.1 mol L^{-1} of tetrabutylammonium tetrafluoroborate $[NBu_4]BF_4$, and the compounds (**1**), (**2**), (**3**) a concentration of 5x10^{-4} mol L^{-1} in 10 ml of CH_2Cl_2. To study the electrochemical oxidation of the heterobimetallic complex [Cp*Ni-s-Ic'-RuCp*] (**3**), to comparison with the monometallic compounds bis(pentamethylcyclopentadienyl)nickel (**1**) and bis(cyclopentadienyl)ruthenium (**2**) (Figure 1).

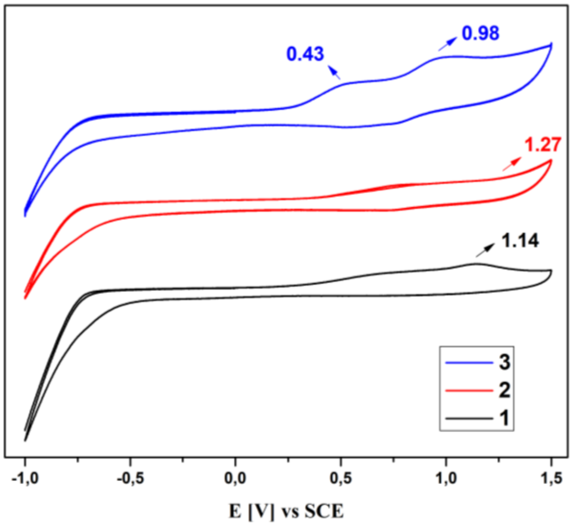


Figure 1: Cyclic voltammetry of compounds (**1**), (**2**) and (**3**) (5x10^{-4}M) in CH_2Cl_2 tetrabutylammonium tetrafluroborate 0.1M, scan rate 0.1 V s^{-1}.

In cyclic voltammetry, the oxidation potential of a compound is an important parameter that provides information about the electrochemical properties of the compound. The oxidation potential is the voltage at which an electroactive species is oxidized, and it reflects the ease with which the species can lose an electron.

In the case of a nickel-ruthenium heterobimetallic compound with oxidation potentials of 0.43 and 0.98 Volts for each metal, respectively, compared to its monometallic analogues with oxidation potentials of 1.14 volts for nickel and 1.27 volts for ruthenium, it can be inferred that the heterobimetallic compound has a lower oxidation potential than its monometallic analogues.

This lower oxidation potential can be attributed to the electronic interactions between the two metals in the heterobimetallic compound. The presence of two different metals in the compound can affect the electronic structure and distribution of electrons, leading to a change in the oxidation potential [15].

The cyclic voltammetry data for the nickel-ruthenium heterobimetallic compound can be related to its catalytic effect on the decomposition temperature of ammonium perchlorate (AP), which is a widely used oxidizer in solid rocket propellants. The decomposition of AP is an exothermic reaction that releases a large amount of heat, and the decomposition temperature is a critical parameter that determines the performance and safety of solid rocket propellants.

It has been shown that the addition of certain transition metal catalysts, such as nickel and ruthenium, can significantly lower the decomposition temperature of AP, thereby improving the combustion efficiency and specific impulse of the propellant. The catalytic effect is believed to be due to the formation of metal-AP complexes that facilitate the transfer of electrons and promote the decomposition reaction [16].

In the case of the nickel-ruthenium heterobimetallic compound, the lower oxidation potential of the compound compared to its monometallic analogues suggests that the compound may have a unique electronic structure that can facilitate the formation of metal-AP complexes and enhance the catalytic effect. Furthermore, the difference in the redox properties of the two metals in the compound can allow for selective activation of certain reactants or intermediates, which would lead to improved catalytic performance.

Catalytic effect

The catalytic properties of the metallocenes (Figure 2) for the thermal decomposition of AP were examined using DSC measurements at a heating rate of 5°C per minute in an N_2 atmosphere in the 140-450°C range. The DSC curves of both AP and the mixture of AP with the labeled compound are presented in Figure 2 and Figures S1-S3 of the Supplementary data.

The mass percentages of (**1**), (**2**), (**3**), and mixture (**1**+**2**)-based BR catalysts were 3 and 5 wt.%, because below these percentages (1 wt%) it has not been carried out significantly the catalytic effect. Figure 2 shows the DSC curves of both AP and the mixture of AP with organometallic compounds.

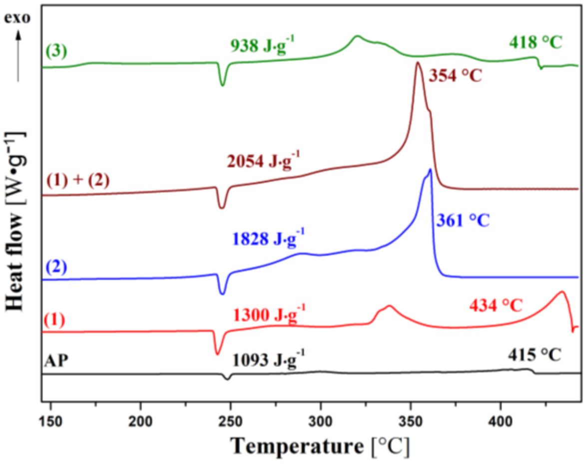


Figure 2: DSC curves for pure AP and different compounds of (**1**), (**2**), (**3**), and mixture (**1**+**2**) + AP (5%wt).

It is well known that during the thermal decomposition of AP, the DSC curves display an endothermic process corresponding to the phase transition of AP at 249°C, which shows little to no shift and a similar profile for different wt.% of compounds (1), (2), (3), and the mixture (1+2) as an additive. This result suggests that the catalysts have a minimal effect on the crystallographic transition temperature of AP. However, the high-temperature degradation (HTD) step of AP at 415°C was significantly affected by adding the catalysts of compounds (**1**), (**2**), (**3**), and the mixture (**1+2**).

In the case where compounds (**1**) and (**3**) were added at 3 and 5 wt.%, the HTD was found to increase, while the heat released decreased, acting as retarding agents (Figure S1 and Figure S3). For compound (**1**), the decomposition temperature at 5 wt.% was obtained at 434°C with a heat release of 1300 J·g^{-1}. Similarly, for compound **(3)**, the maximum shift of the decomposition temperature at 5 wt.% was obtained at 418°C with a heat release of 938 J·g^{-1}.

Regarding compound (**2**), the decomposition temperature at 5 wt.% was observed at 361 °C, with a heat release of 1828 J·g^{-1} (Figure S2). This catalytic behavior is similar to the homo- and heterobimetallic compounds published by our research group (Table 1) [6,17,18].

Most notable is the case when a synergistic effect is observed in the mixture of metallocenes (**1**) and (**2**) on HTD of AP (Figure 3). The mixture (**1**+**2**) shows a decrease in HTD to 354 ºC at 5 wt.%, with a heat release of 2054 J·g^{-1}, producing a left shift by 61 °C compared to pure AP. This result implies that the mixture of species (**1**+**2**) presents an evident catalytic effect on the thermal degradation of AP.

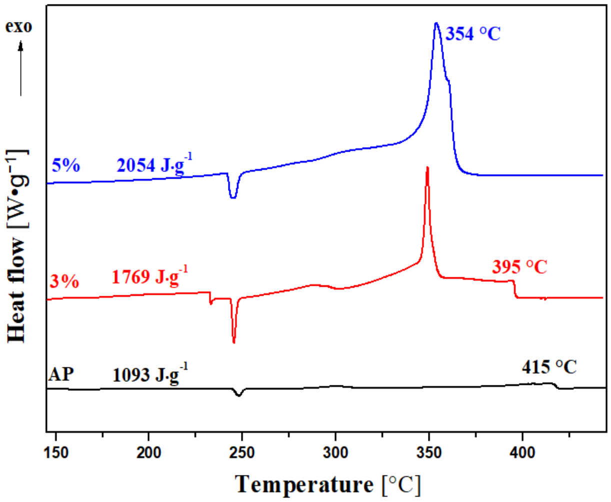


Figure 3: DSC curves of AP with different percentages of Mixture "(**1**+**2**)" + AP.

Finally, the mixture (**1**+**2**) has a higher heat released compared with complexes (**1**), (**2**), and (**3**), even higher than the previously reported ruthenium compounds (Table 1).

Table 1: Effect of the different additives on the thermal degradation of AP.

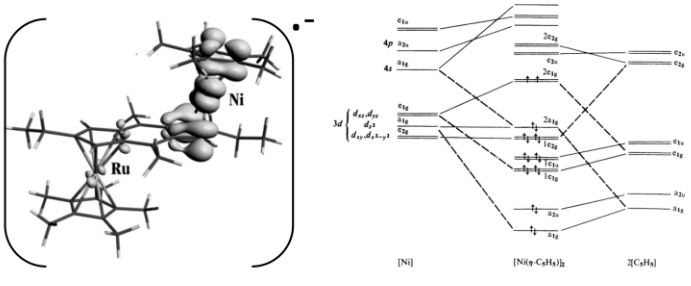
Compounds	**wt [%]**	**HTD of AP (ºC)**	**Heat released (J·g^{-1})**
NH_4ClO_4 (AP)	5	415	1093
[(Cp*)$_2$Ni] **(1)**	5	434	1300
[(Cp*)$_2$Ru] **(2)**	5	361	1828
[Cp*Ni-*s*-Ic'-Cp*Ru] **(3)**	5	418	938
Mixture (**1**+**2**)	5	354	2054
[Cp*Fe-*s*-Ic'-NiCp*] [13]	5	346	1461
[(CO)$_3$Mn-*s*-Ic'-NiCp*] [6]	5	397	965
[(CO)$_3$Mn-*s*-Ic'-RuCp∗] [6]	5	388	1431
[(Cp∗Ru)$_2$-*s*-Ic'] [17]	5	412	669
[(Cp∗Ru)$_2$-*as*-Ic'] [17]	5	347	2048
[(Cp*Ru)$_2$Pen] [17]	5	371	1718
[(Cp*Ru)$_2$-IF] [17]	5	381	1271

As it was reported in the literature [6], the compounds derived from nickel appeared to have poor catalytic effects against the thermal ignition of AP, as was observed for compound (**1**).

If we compare the catalytic activity of (**2**) with the homobimetallic compound [(Cp*)$_2$Ru-*as*-Ic'], it is possible to observe similar behavior, since as is known, the *as*-indacene ligand has little communication between its metal centers, unlike the *s*-indacene ligand. This evidence suggests that both metal fragments in [(Cp*)$_2$Ru-*as*-Ic'] act as independent units like monometallic compounds (**2**).

The commonly accepted electron transfer degradation mechanism for AP comprises the electron transfer from perchlorate (ClO_4^-) to ammonium (NH_4^+), releasing as final products ammonia (NH_3) and perchloric acid ($HClO_4$), where oxygen is generated from $HClO_4$ and then converted to superoxide ($O_2^{\cdot-}$). Finally, these ions in conjunction with other gaseous products contribute to the NH_3 decomposition (Figure 4).

Previous ESR studies and DFT calculations have shown that heterobimetallic compounds derived from *s*-indacene (Figure 4a) [19] can be reduced by electron-rich olefins (EROs) to form corresponding radical anions ($A^{\cdot-}$). These radical heterobimetallic anions exhibit dissymmetric spin distribution, indicating that the two metals have different electrophilic properties [20], as observed through previous electrochemical studies (*vida supra*). In compound (**3**), the difference in electronegativity between the metal centers leads to a more dissymmetric spin distribution towards the more electronegative metallic moiety, which is the nickelocene fragment. This fragment's withdrawing effect causes an increase of spin density over its ligands (Cp* and the nearby five-member ring of the indacenyl ligand), suggesting that this molecule acts as an electron acceptor. The resulting anionic species ($A^{\cdot-}$) is stabilized by the delocalized ligand *s*-indacene, leading to a retarding effect, similar to the action of antioxidant agents.



(a) (b)

Figure 4: **(a)** Calculated spin density distribution of the heterobimetallic Ru-Ni radical anion (taken from the reference [22]). **(b)** Simplified molecular orbital scheme for nickelocene (taken from the reference [23]).

On the other hand, the synergistic effect presented by the mixture (**1**+**2**) could be explained because the metal centers are not connected by a bridging ligand, consequently the electron transfer from the ruthenocene would be received by the half-filled orbitals of the antibonding ($2e_{1g}$) nickelocene (Figure 4b) [20], which would destabilize the nickelocene and decomposing it, promoting and accelerating electron transfer towards the formation of $O_2^{\cdot-}$ (Figure 5).

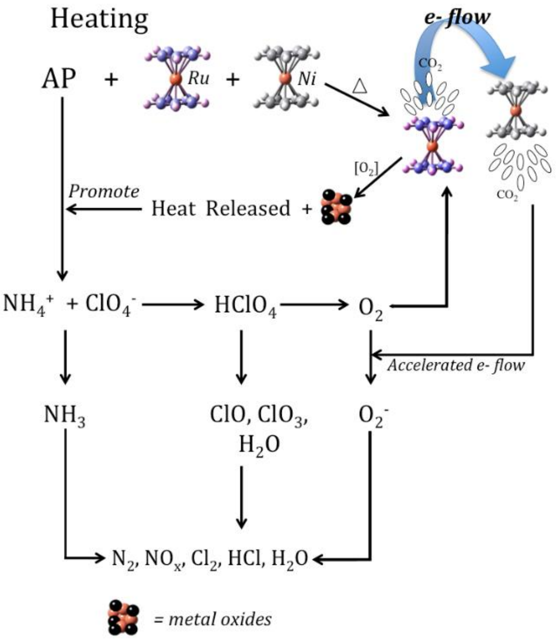


Figure 5: Possible AP catalytic thermal decomposition process.

CONCLUSION

In conclusion, the catalytic properties of bis(pentamethylcyclopentadienyl) nickel (**1**), bis(cyclopentadienyl)ruthenium (**2**), and heterobimetallic complex [Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacene)NiCp] (**3**) were evaluated for the thermal decomposition of ammonium perchlorate (AP). The results showed that the addition of compounds (**1**), (**2**), (**3**), and the mixture (**1**+**2**) as additives had a significant effect on the high-temperature degradation (HTD) step of AP at 415°C. The mixture of metallocenes (**1**) and (**2**) showed a synergistic effect, producing a left shift by 61°C compared to pure AP, with a higher heat release compared with the individual complexes. This suggests that the mixture (**1**+**2**) presents an evident catalytic effect on the thermal degradation of AP. The findings of this study could have practical implications in the development of efficient catalysts for the combustion of solid rocket propellants.

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REFERENCES

1. J. Gaete, J.L. Arroyo, A. Norambuena, G. Abarca, C. Morales-verdejo, Mechanistic Insights into the Thermal Decomposition of Ammonium Perchlorate : The Role of Amino-Functionalized Magnetic Nanoparticles, Inorg. Chem. 61 (2022) 1447–1455. doi:10.1021/acs.inorgchem.1c03121.
2. J. Gaete, C. Valdebenito, Y. Dibdalli, J.L. Arroyo, Á. Norambuena, F. Valenzuela, C. Basualto, G. Abarca, C. Morales-Verdejo, Superparamagnetic energetic nanoparticles : a surface self - propagation pathway for the thermal decomposition of ammonium perchlorate, J. Therm. Anal. Calorim. (2023). doi:10.1007/s10973-022-11885-5.
3. L. Jiang, M. Liu, L. Xu, T. Dong, J. Li, G. Zhang, Synthesis and Characterization of a Dinuclear Nitrogen-Rich Ferrocenyl Ligand and Its Ionic Coordination Compounds and Their Catalytic Effects During Combustion, ZAAC - J. Inorg. Gen. Chem. 645 (2019) 92–100. doi:10.1002/zaac.201800417.
4. M. Usman, L. Wang, H. Yu, F. Haq, R. Liang, R. Summe Ullah, A. Khan, A. Nazir, T. Elshaarani, K. Naveed, Inorganica Chimica Acta Synthesis , anti-migration properties and burning rate catalytic properties of ferrocene-based compounds, Inorganica Chim. Acta. 495 (2019) 118958. doi:10.1016/j.ica.2019.118958.
5. M. Usman, H. Yu, L. Wang, P.A. Zhizhko, D.A. Lemenovskiy, D.N. Zarubin, A. Khan, K. Naveed, Synthesis of ferrocenylated-aminopyridines and ferrocenylated- aminothiazoles and their anti-migration and burning rate catalytic properties, J. Organomet. Chem. 920 (2020) 121336. doi:10.1016/j.jorganchem.2020.121336.
6. J.L. Arroyo, A. Norambuena, H. Reyes, C. Valdebenito, G. Abarca, D.M. Carey, C. Morales-verdejo, Heterobimetallic Catalysts for the Thermal Decomposition of Ammonium Perchlorate : Efficient Burning Rate Catalysts for Solid Rocket Motors and Missiles, Inorg. Chem. 60 (2021) 1436–1448. doi:10.1021/acs.inorgchem.0c02639.
7. K. Ghosh, S. Behera, A. Kumar, B.G. Padale, D.G. Deshpande, A. Kumar, M. Gupta, Studies on aluminized, high burning rate, Butacene® based, composite propellants, Cent. Eur. J. Energ. Mater. 11 (2014) 323–334.
8. Á. Norambuena, P. Gutiérrez, J.L. Arroyo, H. Reyes, C. Morales-verdejo, Studies of burning rate and pressure exponent of a new combustion catalyst derived from p-phenylene, J. Energ. Mater. (2021). doi:10.1080/07370652.2021.1942329.
9. S. Chaturvedi, P.N. Dave, Solid propellants : AP/HTPB composite propellants, Arab. J. Chem. 12 (2019) 2061–2068. doi:10.1016/j.arabjc.2014.12.033.
10. M.E. Smith, Synthesis, Characterization, and Reactivity of Pentamethylcyclopentadienyl Complexes of Divalent Cobalt and Nickel, 1993. https://escholarship.org/uc/item/0vg5n9kq#author.
11. S. Trupia, A. Nafady, W.E. Geiger, Electrochemical Preparation of the Bis(ruthenocenium) Dication, Inorg. Chem. 42 (2003) 5480–5482. doi:10.1021/ic030146+.
12. C. Morales-Verdejo, I. Martinez, D. Mac-Leod Carey, I. Chavez, J.M. Manríquez, D. Matioszek, N. Saffon, A. Castel, P. Rivière, E. Molins, Synthesis and structure of some heterobimetallic complexes having a polyalkyl-s-indacenyl spacer, Inorganica Chim. Acta. 394 (2013). doi:10.1016/j.ica.2012.09.040.
13. C. Morales-Verdejo, M.B. Camarada, J.L. Arroyo, P. Povea, G. Carreño, J.M. Manriquez, Effect of the homo- and heterobimetallic compounds derived from s-indacene on the thermal decomposition of ammonium perchlorate: Potential applications as burning rate catalysts, J. Therm. Anal. Calorim. 131 (2018) 353–361. doi:10.1007/s10973-017-6534-7.
14. J.L. Arroyo, P. Povea, R. Faúndez, M.B. Camarada, C. Cerda-cavieres, G. Abarca, J.M. Manriquez, C. Morales-Verdejo, Influence iron-iron distance on the thermal decomposition of ammonium perchlorate . New catalysts for the highly efficient combustion of solid rocket propellant, J. Organomet. Chem. 905 (2020) 121020. doi:10.1016/j.jorganchem.2019.121020.
15. P. Aguirre-Etcheverry, D. O'Hare, Electronic communication through unsaturated hydrocarbon bridges in homobimetallic organometallic complexes, Chem. Rev. 110 (2010) 4839–4864. doi:10.1021/cr9003852.
16. B.U. Amin, H. Yu, L. Wang, A. Nazir, S. Fahad, F. Haq, S. Mahmood, R. Liang, A. Uddin, T. Lin, Recent advances on ferrocene-based compounds and polymers as a burning rate catalysts for propellants, J. Organomet. Chem. 921 (2020) 121368. doi:10.1016/j.jorganchem.2020.121368.
17. Y. Dibdalli, C. Osorio-gutierrez, J.L. Arroyo, M.K. Amshumali, G. Abarca, C. Morales-Verdejo, Catalytic Effects of Ruthenocene Bimetallic Compounds Derived from Fused Aromatic Ring Ligands on the Main Oxidizing Agent for Solid Rocket Motor, J. Braz. Chem. Soc. 33 (2022) 491–497. doi:10.21577/0103-5053.20210168.
18. Y. Dibdalli, J. Gaete, C. Valdebenito, J. Luis, I. Martínez, G. Abarca, C. Morales-verdejo, Bimetallic ruthenium compound derived from 6 , 12-dihydroindeno [1 ,2-b] fluorene ligand as burning rate catalyst for solid rocket motor propellant, J. Organomet. Chem. 973–974 (2022) 122408. doi:10.1016/j.jorganchem.2022.122408.
19. D. MacLeod Carey, C. Adams, A. Muñoz-Castro, C. Morales-Verdejo, J.F. Araneda, I. Chavez, J.M. Manríquez, A. Castel, P. Rivière, M. Rivière-Baudet, D. Matioszek, R. Septelean, I. Martinez, R. Arratia-Pérez, A new method to radical anions derived from s-Indacene organobimetallic complexes, their ESR characterization, Inorganica Chim. Acta. 392 (2012). doi:10.1016/j.ica.2012.05.033.
20. P.W. Jolly, Comprehensive Organometallic Chemistry, Elsevier, 1982. doi:10.1016/B978-008046518-0.00073-8.