Carbon black-supported platinum and cobalt nanoparticles for the catalytic hydrolysis of ammonia borane: A comparative performance study

Leonardo R. Leal (G)*[1], Débora M. Fontes (G)[1], Tiago A. Silva (PQ)[1], Renata P. L. Moreira (PQ)[1]

[1] **leonardo.leal@ufv.br; tiago.a.silva@ufv.br**
[1]Department of Chemistry, Federal University of Viçosa, Viçosa, Minas Gerais, Brazil.

Platinum and cobalt nanoparticles supported on carbon black (PtNPs/CB and CoNPs/CB) were synthesized via chemical reduction with sodium borohydride and tested as heterogeneous catalysts for hydrogen generation from ammonia borane (AB). The PtNPs/CB catalyst achieved complete hydrogen release (H_2/NH_3BH_3 = 3:1) within 200 s, with a turnover frequency (TOF) of 5.53 mol $H_2 \cdot mol^{-1}$ Pt$\cdot min^{-1}$ and a hydrogen generation rate (HGR) of 5807.8 mL$\cdot min^{-1} \cdot g^{-1}$. In contrast, CoNPs/CB exhibited lower activity (TOF = 0.0474 mol $H_2 \cdot mol^{-1}$ Co$\cdot min^{-1}$; HGR = 545.5 mL$\cdot min^{-1} \cdot g^{-1}$), with incomplete hydrogen release. Both catalysts contained 4 wt% of metal (4.37 mg Pt; 1.32 mg Co). Compared to commercial Pt/C benchmarks, the PtNPs/CB showed competitive performance under mild aqueous conditions. The modest TOF values for both systems suggest limited nanoparticle dispersion or partial surface passivation, possibly due to incomplete reduction or aggregation. Although CoNPs/CB showed slower kinetics, its abundance, low cost, and potential for electronic modulation (e.g., via nitrogen doping or alloying) make it a promising platform for further optimization. These results confirm the superior catalytic performance of Pt under mild conditions and highlight carbon black as a cost-effective support that promotes electronic conductivity and nanoparticle stabilization.

Keywords: *hydrogen evolution; non-noble catalysts; metal–support synergy; carbon-supported H_2 catalysts*

Introduction

Ammonia borane (NH_3BH_3) is a promising hydrogen storage material due to its high gravimetric hydrogen content and controlled hydrolysis under mild aqueous conditions [1]. Platinum-based catalysts are highly active for AB dehydrogenation but are limited by cost and scarcity. As such, transition metal alternatives such as cobalt (Co) have been explored, although with lower activity. Conductive carbon supports like carbon black (CB) play a crucial role in enhancing dispersion, electron transfer, and stability of metal nanoparticles [1]. This study compares the catalytic behavior of PtNPs/CB and CoNPs/CB systems prepared via sodium borohydride reduction and evaluated under identical conditions. By analyzing both total turnover number (TTON) and TOF over time, this work aims to elucidate the performance gap between noble and non-noble systems and identify pathways for catalyst improvement.

Experimental

Synthesis and immobilization of nanoparticles on carbon black

First, a support suspension was prepared by dispersing 10 mg of carbon black (CB) in 3.0 mL of deionized water under magnetic stirring for 10 minutes. Subsequently, 22.4 µmol of the respective metal precursor salt (H_2PtCl_2 or $Co(NO_3)_2$) was added to the CB suspension. The mixture was stirred for an additional 15 minutes at room temperature to ensure adequate impregnation of metal ions onto the support. Chemical reduction was then initiated by the dropwise addition of a freshly prepared aqueous solution of sodium borohydride, prepared by dissolving 17 mg of $NaBH_4$ in 2.0 mL of deionized water. The reaction was allowed to proceed for 15 minutes under continuous stirring to promote complete nanoparticle formation. The resulting nanocomposite was subsequently purified by two cycles of centrifugation and washing with deionized water, each cycle lasting 20 minutes, to remove residual ions and reaction byproducts. This procedure yielded monodisperse Pt or Co nanoparticles anchored onto the carbon black support.

Hydrogen Evolution from Ammonia Borane Hydrolysis

The catalytic activity of the prepared materials was evaluated by measuring the volume of hydrogen generated from the hydrolysis of ammonia borane (AB) using a water-displacement method. In a typical experiment, the catalyst was transferred to a two-necked reaction flask maintained at a constant temperature within a water bath. After the system was sealed, the reaction was initiated by injecting an aqueous solution of AB with a concentration of 590 mM prepared in 1.0 mL of deionized water into the flask containing the catalyst. The volume of evolved hydrogen was recorded at regular time intervals using an inverted burette, and the reaction was monitored until gas evolution ceased.

Results and Discussion

The catalytic performance comparison between PtNPs and CoNPs supported on carbon black (CB), both synthesized via chemical reduction with $NaBH_4$, revealed substantial differences in ammonia borane (AB) hydrolysis. As shown in Figure 1, PtNPs/CB achieved complete stoichiometric hydrogen release (H_2/AB = 3:1) within approximately 200 seconds, with a hydrogen generation rate (HGR)

of 5807.8 mL·min^{-1}·g^{-1} and a turnover frequency (TOF) of 5.53 mol H_2·mol^{-1} Pt·min^{-1}. In contrast, CoNPs/CB exhibited much lower catalytic activity, with a TOF of 0.0474 mol H_2·mol^{-1} Co·min^{-1} and an HGR of 545.5 mL·min^{-1}·g^{-1}, reflecting slower reaction kinetics and incomplete hydrogen release. The superior performance of PtNPs/CB is consistent with commercial Pt/C benchmarks in terms of HGR.

Molar H_2/AB ratio as function of time

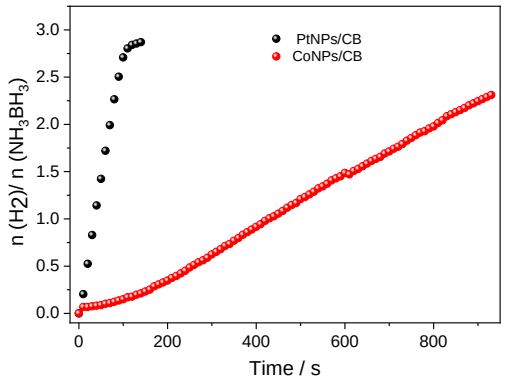

Figure 1. Plot of time vs n(H_2)/n(NH_3BH_3) for the hydrolysis of ammonia borane catalyzed by PtNPs/CB and CoNPs/CB. ([AB] = 590 mM, [PtNPs/CB] = 22.4 mM, [CoNPs/CB] = 22.4 mM, T = 25 °C ±1 °C).

Total Turnover number (TTON) and hydrogen evolution of PtNPs/CB

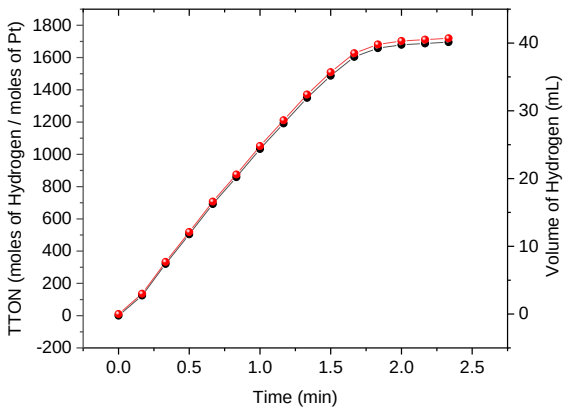

Figure 2. Total turnover number (TTON) and volume of hydrogen(mL) vs time (min) plot for the hydrolysis of ammonia borane catalyzed by PtNPs/CB. TTON is defined as the molar ratio of evolved H_2 to catalyst loading (mol H_2 / mol catalyst).

The Total Turnover Number (TTON) analysis presented in Figure 2 shows a rapid and continuous increase in the amount of hydrogen evolved per mole of Pt until saturation, confirming the high catalytic efficiency of PtNPs/CB. The catalyst achieved a TTON above 1800 under the tested conditions, reflecting not only its high intrinsic activity but also good accessibility of active sites. Despite the limitations observed, carbon black effectively served as a support by improving the structural stability of the catalysts.

Total Turnover number (TTON) and hydrogen evolution of CoNPs/CB

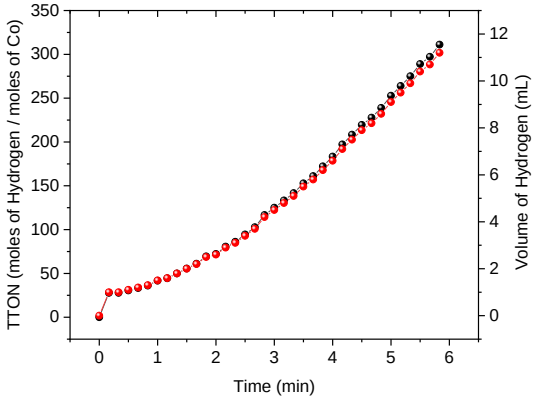

Figure 3. Total turnover number (TTON) and volume of hydrogen (mL) vs time (min) plot for the hydrolysis of ammonia borane catalyzed by CoNPs/CB. TTON is defined as the molar ratio of evolved H_2 to catalyst loading (mol H_2 / mol catalyst).

Figure 3 reveals the comparatively lower catalytic performance of CoNPs/CB, with TTON values below 300 and incomplete hydrogen evolution over time. These results are consistent with the known limitations of undoped cobalt catalysts, which often exhibit poor electronic conductivity and limited hydrogen evolution kinetics. Thus, although the activity of CoNPs/CB is modest, its low cost, abundance, and the potential for structural enhancement, such as doping or alloying with Pt, make it a viable platform for further development. Despite the lower efficiency of CoNPs/CB, its cost-effectiveness and abundance make it a candidate for further optimization. Strategies such as nitrogen doping or the design of Co–Pt bimetallic catalysts could enhance its activity by modulating the electronic structure of surface atoms.

Conclusion

The catalytic evaluation confirmed the superior performance of PtNPs/CB for AB hydrolysis, achieving complete H_2 evolution rapidly and exhibiting high TOF and TTON values. CoNPs/CB showed comparatively lower activity, consistent with literature reports for undoped cobalt systems. However, considering its low cost and the possibility of electronic and structural tuning, CoNPs/CB remains a promising candidate for further investigation. The use of carbon black as a support was effective in stabilizing nanoparticles and facilitating charge transport. Ongoing work will focus on the development of Co–Pt bimetallic catalyst systems to enhance catalytic efficiency under ambient conditions.

Acknowledgments

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References

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