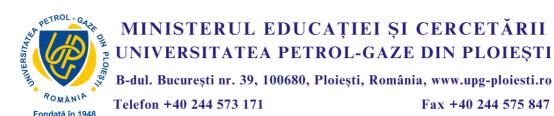


INSTITUȚIA ORGANIZATOARE DE STUDII UNIVERSITARE DE DOCTORAT UNIVERSITATEA PETROL-GAZE DIN PLOIEȘTI DOMENIUL FUNDAMENTAL – ȘTIINȚE INGINEREȘTI DOMENIUL DE DOCTORAT – INGINERIE CHIMICĂ

TEZĂ DE DOCTORAT SISTEME CATALITICE PENTRU SINTEZA CARBONATULUI DE GLICERINĂ

Autor: Ing. Mirna, Léa CHARIF

Conducător științific: Prof. univ. dr. ing. CIUPARU Dragoș-Mihael





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Nr. Decizie 564 din 23.07.2025

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DOCTORAL THESIS

CATALYTIC SYSTEMS FOR THE SYNTHESIS OF GLYCEROL CARBONATE

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Decision No. 564 dated 23.07.2025

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Ploiești 2025

Abstract

This doctoral research delivers an in-depth investigation into the design, synthesis, and performance of advanced heterogeneous catalytic systems for the direct carboxylation of glycerol with carbon dioxide (CO₂) to produce glycerol carbonate (GC), a high-value, bio-based chemical with broad industrial applications. The study is driven by the dual need to valorize surplus glycerol, a by-product of biodiesel production, and to utilize CO₂ as a renewable carbon source, addressing pressing global concerns around waste management and greenhouse gas emissions.

The reaction between glycerol and CO₂ is both thermodynamically and kinetically challenging due to CO₂'s chemical inertness and the formation of water as a by-product, which shifts the equilibrium unfavorably. To overcome these limitations, this research focuses on developing robust, selective, and recyclable heterogeneous catalysts with tailored surface properties that enhance CO₂ activation, glycerol adsorption, and GC formation while suppressing side reactions and catalyst deactivation.

Two main categories of catalysts were synthesized. The first consisted of graphitic carbon nitride (g-C₃N₄) doped with phosphorus (P), sulfur (S), lithium (Li), and magnesium (Mg), prepared by thermal polycondensation. The second group comprised mixed metal oxides incorporating titanium (Ti), aluminum (Al), chromium (Cr), iron (Fe), and magnesium (Mg), synthesized using chemical co-precipitation. The resulting materials were comprehensively characterized using a combination of XRD, SEM-EDX, BET, TGA-DTG, XPS, FTIR and CO₂-TPD to assess their structural, morphological, textural, thermal, and surface chemical properties.

XRD analysis confirmed that the graphitic structure of g-C₃N₄ was preserved, while the broadening and shifting of diffraction peaks due to doping indicated successful dopant integration and the creation of structural defects. For the metal oxide catalysts, the diffraction patterns revealed the presence of nanocrystalline phases like MgTi₂O₅, TiO₂, Ti₃O₂, MgO, and various doped mixed oxides, verifying the formation of multi-phase materials that promote diverse catalytic active sites. SEM revealed well-developed microstructures: layered sheets for g-C₃N₄ and spherical/agglomerated morphologies for oxides. EDX mapping confirmed homogeneous dispersion of dopants, essential for uniform catalytic activity.

BET surface area analysis demonstrated significant enhancements in mesoporosity and surface area following doping. Notably, Li-doped g-C₃N₄ nearly doubled the surface area compared to undoped samples, while TiAlMgOx achieved the highest surface area and pore volume among the oxides (119.43 m²/g and 0.345 cm³/g), facilitating better CO₂ diffusion and glycerol interaction. TGA-DTG confirmed thermal stability above 450 °C for all catalysts, ensuring their durability under reaction conditions. XPS data showed the presence of catalytically active metal species and strong metal—oxygen bonds, indicating well-integrated dopants and stable oxidation states. FTIR spectra supported successful incorporation of dopants into the g-C₃N₄ framework, with clear shifts in N–H and C–N vibrations reflecting electronic and structural reorganization.

Catalytic tests for GC synthesis under varying conditions highlighted Mg-doped g-C₃N₄ (MgPSCN) and TiAlMgOx as the most efficient systems. Their high activity was attributed to enhanced surface basicity, synergistic dopant effects, and optimized porosity. Using response surface methodology (RSM), the process was optimized for key variables including temperature, CO₂ pressure, catalyst loading, reaction time, and choice of dehydrating agent. The ideal conditions are 250 °C, 7 bar CO₂ pressure, 50% catalyst amount, 4 hours reaction time, and acetonitrile as a dehydrating agent, led to a maximum glycerol conversion of 68.72% and GC yield of 44.90% with MgPSCN. TiAlMgOx also demonstrated excellent GC selectivity and thermal resilience, maintaining performance at elevated temperatures due to balanced acid–base properties and higher magnesium content. In contrast, Fe-Ti-Mg showed declining performance due to thermally induced side reactions, and Cr-Ti-Mg underperformed due to its strong acidity, which favored by-product formation.

Catalyst reusability was also examined. MgPSCN retained its structure and chemical integrity after four consecutive cycles, although GC yield decreased by approximately 20% due to surface fouling from reaction by-products. XRD and XPS confirmed the absence of structural degradation or leaching, validating the catalyst's long-term stability.

Ultimately, this research proves that catalytic performance in GC synthesis is strongly influenced by surface basicity, dopant-induced electronic tuning, and mesoporosity. The developed catalysts not only exhibit high conversion and selectivity but also show excellent stability and reusability, making them promising candidates for scalable, eco-friendly applications in CO₂ capture and utilization, biodiesel waste valorization, and broader green chemical manufacturing.