MINISTERUL EDUCAȚIEI ȘI CERCETĂRII
UNIVERSITATEA PETROL-GAZE DIN PLOIEȘTI
B-dul. București nr. 39, 100680, Ploiești, România, www.upg-ploiesti.ro
Telefon +40 244 573 171 Fax +40 244 575 847

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

Ploiești 2025

MINISTERUL EDUCAȚIEI ȘI CERCETĂRII
UNIVERSITATEA PETROL-GAZE DIN PLOIEȘTI
B-dul. București nr. 39, 100680, Ploiești, România, www.upg-ploiesti.ro
Telefon +40 244 573 171 Fax +40 244 575 847

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

Nr. Decizie 564 din 23.07.2025

Comisia de doctorat:

Președinte	Prof. univ. habil. dr. ing. Răzvan George RÎPEANU	de la	Universitatea Petrol-Gaze din Ploiești
Conducător științific	Prof. univ. dr. ing. Dragoș Mihael CIUPARU	de la	Universitatea Petrol-Gaze din Ploiești
Referent oficial	Prof. univ. dr. ing. Gabriela CÂRJĂ	de la	Universitatea Tehnică Gheorghe Asachi din Iași
Referent oficial	Conf. univ. dr. ing. Ionuț BANU	de la	Universitatea Națională de Știință și Tehnologie POLITEHNICA București
Referent oficial	Prof. univ. habil. dr. ing. Diana-Luciana CURSARU	de la	Universitatea Petrol-Gaze din Ploiești

Ploiești 2025

MINISTERUL EDUCAȚIEI ȘI CERCETĂRII
UNIVERSITATEA PETROL-GAZE DIN PLOIEȘTI
B-dul. București nr. 39, 100680, Ploiești, România, www.upg-ploiesti.ro
Telefon +40 244 573 171 Fax +40 244 575 847

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

DOCTORAL THESIS

CATALYTIC SYSTEMS FOR THE SYNTHESIS OF GLYCEROL CARBONATE

Author: Ing. Mirna, Léa CHARIF

Scientific supervisor: Prof. univ. dr. ing. CIUPARU Dragoș-Mihael

Decision No. 564 dated 23.07.2025

Doctoral committee:

Chairman	Prof. univ. habil. dr. ing. Răzvan George RÎPEANU	from	Universitatea Petrol-Gaze din Ploiești
Scientific supervisor	Prof. univ. dr. ing. Dragoș Mihael CIUPARU	from	Universitatea Petrol-Gaze din Ploiești
Official reporter	Prof. univ. dr. ing. Gabriela CÂRJĂ	from	Universitatea Tehnică Gheorghe Asachi din Iași
Official reporter	Conf. univ. dr. ing. Ionuț BANU	from	Universitatea Națională de Știință și Tehnologie POLITEHNICA București
Official reporter	Prof. univ. habil. dr. ing. Diana-Luciana CURSARU	from	Universitatea Petrol-Gaze din Ploiești

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 (CO_2) 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 CO_2 as a renewable carbon source, addressing pressing global concerns around waste management and greenhouse gas emissions.

The reaction between glycerol and CO_2 is both thermodynamically and kinetically challenging due to CO_2'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 CO_2 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-C_3N_4) 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 CO_2-TPD to assess their structural, morphological, textural, thermal, and surface chemical properties.

XRD analysis confirmed that the graphitic structure of g-C_3N_4 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 $MgTi_2O_5$, TiO_2, Ti_3O_2, 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-C_3N_4 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-C_3N_4 nearly doubled the surface area compared to undoped samples, while TiAlMgOx achieved the highest surface area and pore volume among the oxides (119.43 m^2/g and 0.345 cm^3/g), facilitating better CO_2 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-C_3N_4 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-C_3N_4 (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, CO_2 pressure, catalyst loading, reaction time, and choice of dehydrating agent. The ideal conditions are 250 °C, 7 bar CO_2 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 CO_2 capture and utilization, biodiesel waste valorization, and broader green chemical manufacturing.