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Department of Materials Science & Engineering
UNIVERSITY OF IOANNINA

Catalytic performance and stability of Ru on Ce-based Aminoclay carriers for Sabatier reaction

A. Kaloudi[1], C. Drosou[2], K. Spyrou[1], P. Zygouri[1], I. V. Yentekakis[2,3], D. P. Gournis[1,2*]

[1]Department of Materials Science and Engineering, University of Ioannina, Ioannina, Greece.
[2]School of Chemical & Environmental Engineering, Technical University of Crete, Chania, Greece.
[3]Institute of GeoEnergy, Foundation for Research and Technology-Hellas (FORTH/IG), Chania, GR.

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Motivation

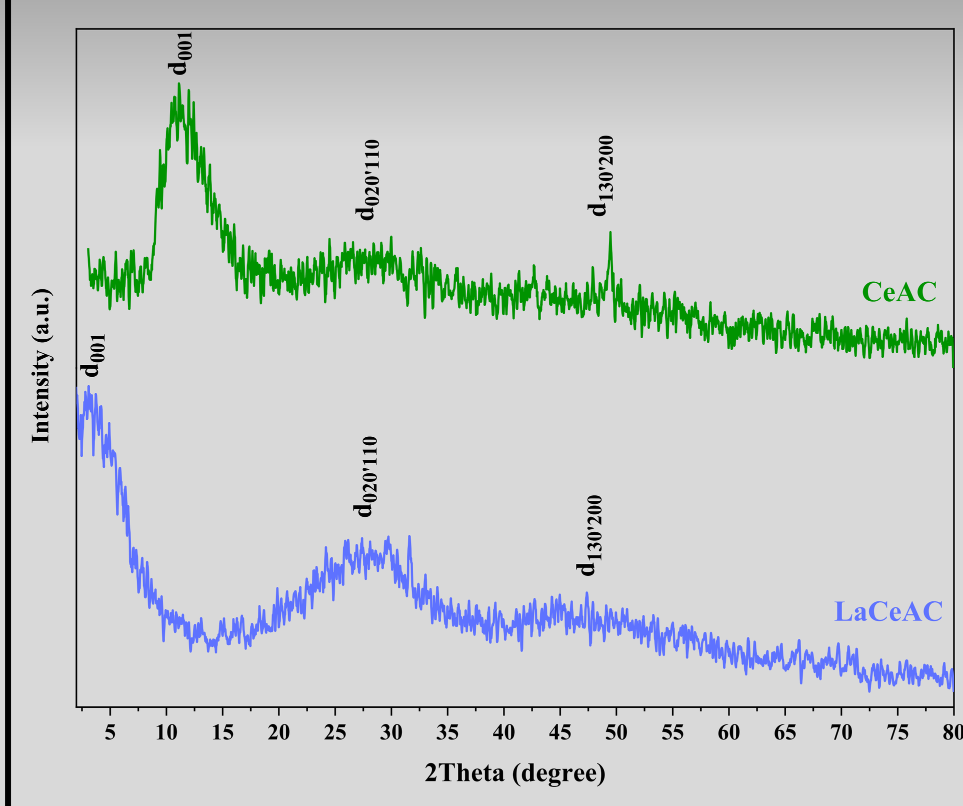
Carbon dioxide (CO_2) is a colorless, and odorless greenhouse gas (GHG) with a faint acid taste. Over the past years, CO_2 concentrations in atmosphere have increased by 30%. As a result, the global surface temperature increased from 0.4 to 0.8 °C. The catalytic hydrogenation of CO_2 to produce CH_4, also known as Sabatier reaction ($CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$; ΔH_0= -164.7 kJ/mol) is considered an extremely important route for CO_2 recycling, with Ni and Ru are among the most active Sabatier catalysts. In this regard, cerium and lanthanum/cerium based synthetic Aminoclay analogues were prepared, using a green, facile, and cost-effective room-temperature sol-gel-based synthetic method, as carriers of Ru nanoparticles (**Ru/CeAC, Ru/LaCeAC**). The performance of this new class of catalysts was investigated under CO_2 hydrogenation conditions were found to be highly active and selective towards CH_4 production.

Design of CeAC & LaCeAC carriers

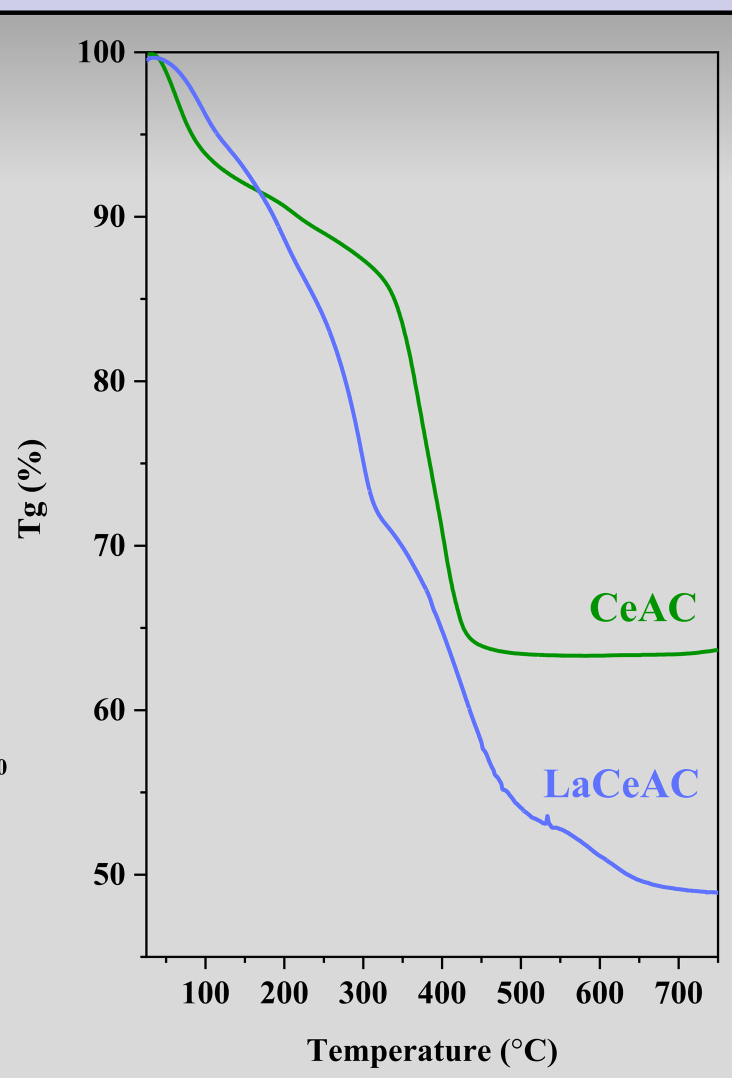
For the preparation of lanthanum-cerium synthetic aminoclay (**LaCeAC**), 1.81 mmol of $CeCl_3 \cdot 7H_2O$ and 1.81 mmol of $La(NO_3)_3 \cdot 6H_2O$ were added in 20 ml ethanol, followed by stirring at room temperature. After 10 min of stirring, 5.85 mmol of N-[3-(Trimethoxy silyl) propyl] ethylenediamine, was added dropwise. The solution remained under continuous stirring for 24 h. A gel-type material obtained after reaction was recovered by centrifugation followed by washing with ethanol. Finally, the sample dried in the oven at 40 °C overnight.
Cerium synthetic aminoclay (**CeAC**) was also prepared according to the previous procedure using 3.62 mmol Cerium chloride heptahydrate ($CeCl_3 \cdot 7H_2O$).

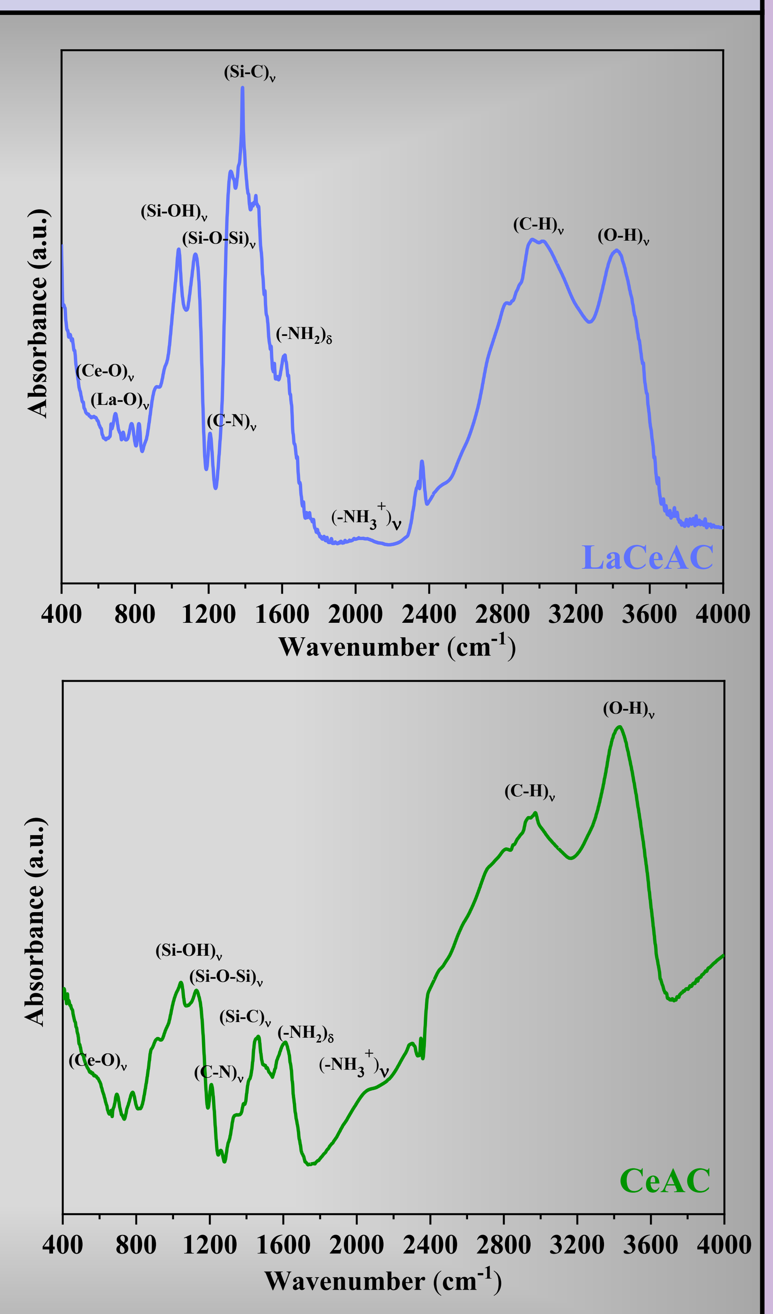
LaCeAC CeAC

Structural characterization



The basal spacing at d_{001}=27 Å for the LaCeAC and d_{001}=8 Å for CeAC, respectively, indicates the thickness of the regularly layered unit clay structure with a bilayer arrangement of propylamino groups.

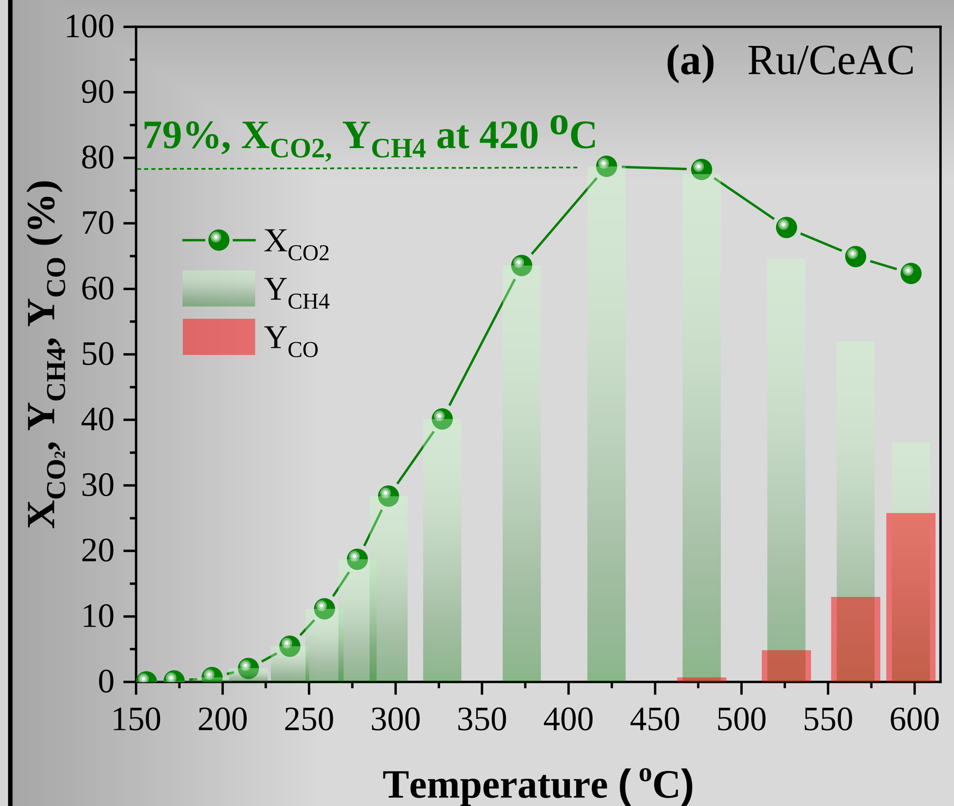


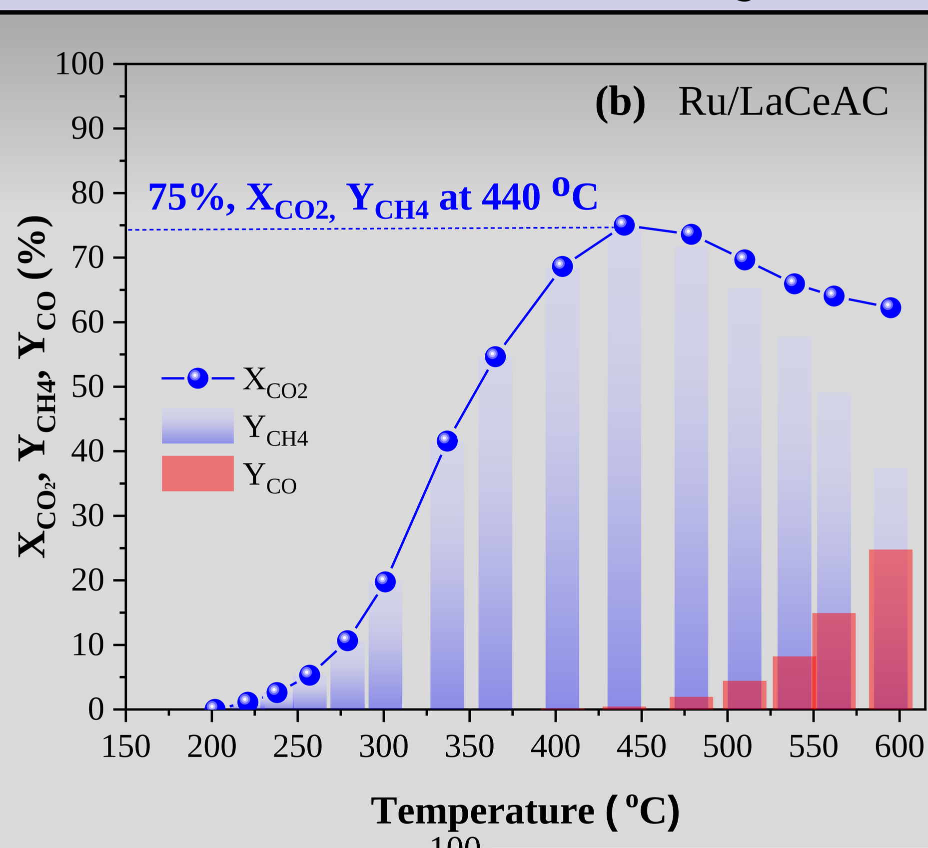


Design of Ru/CeAC and Ru/LaCeAC catalysts

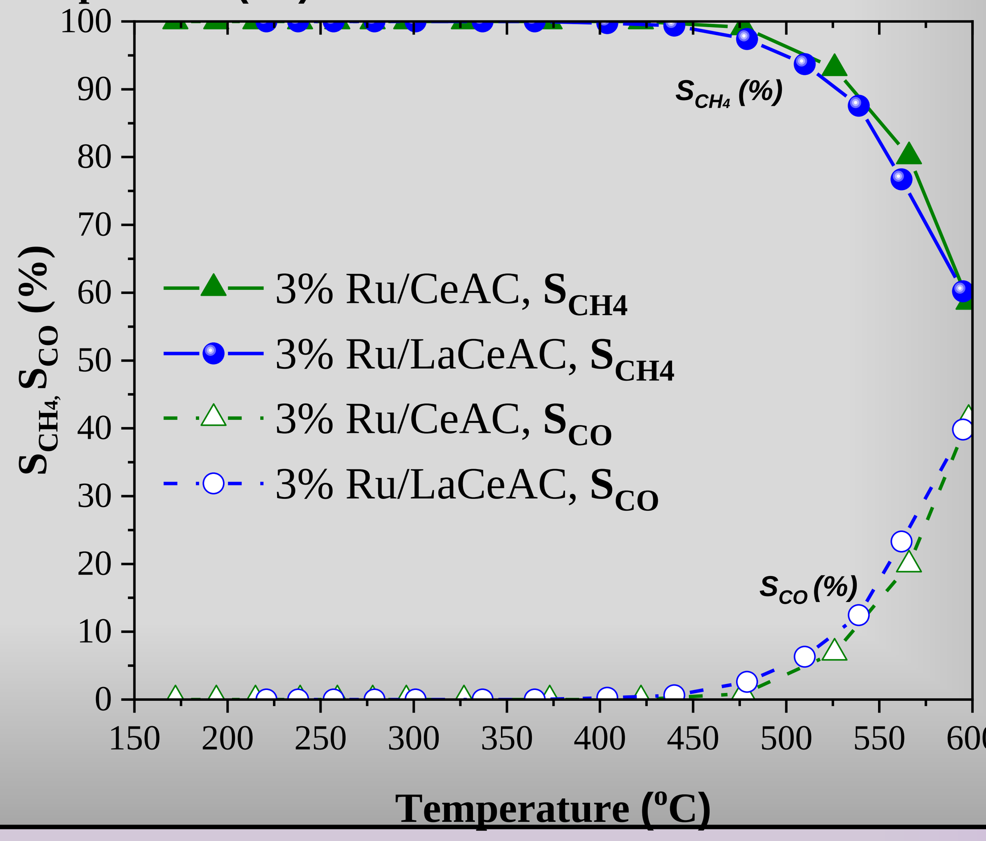
Ruthenium was incorporated on Ce-based aminoclay supports using the conventional wet impregnation method. Appropriate amounts of Ce-based aminoclay were impregnated by specific volume of a Ruthenium (III) nitrosylnitrate solution to obtain a Ru loading of 3%. Then, pH was adjusted to a value of 6 by adding NH_3 solution. The slurry was dried under continuous stirring at 80 °C. The resulting material was further dried at 110 °C overnight and then was calcinated at 450 °C for 1 h.

Ru/CeAC and Ru/LaCeAC catalysts



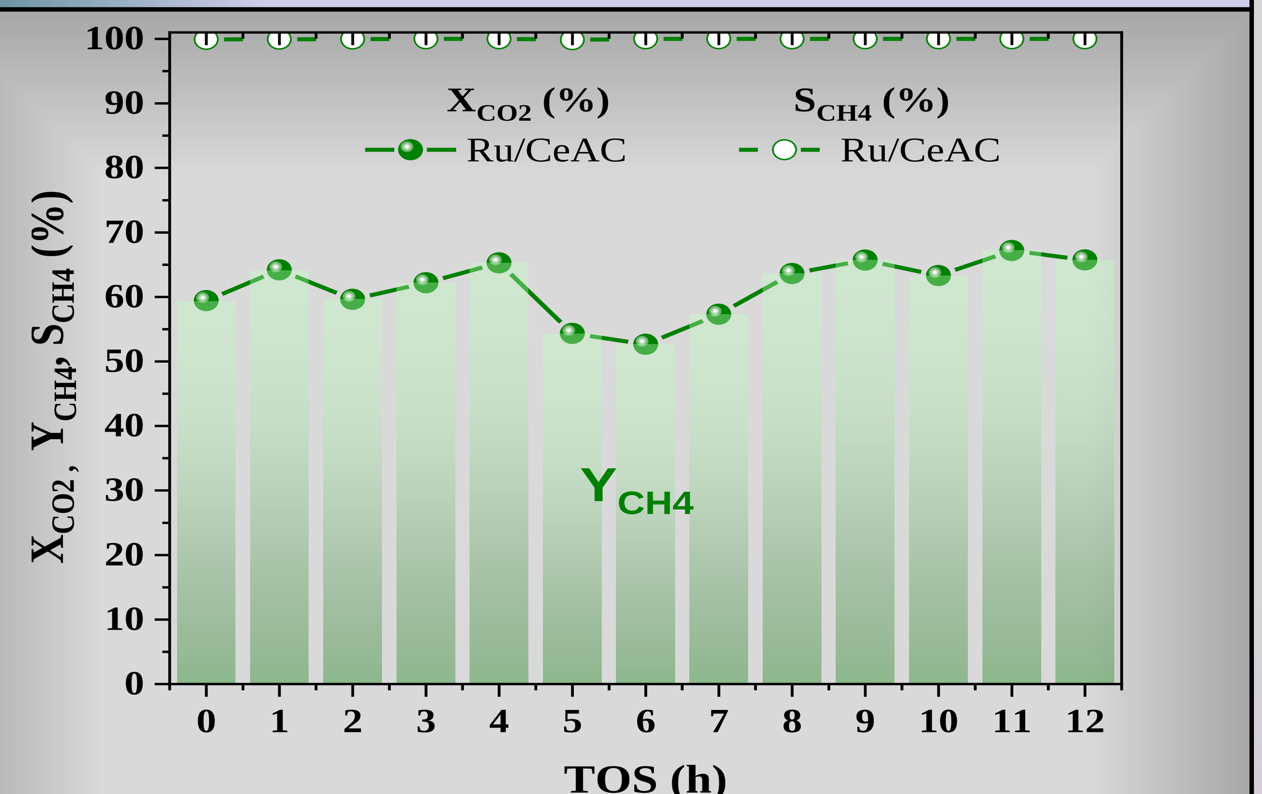


CO_2 conversion (X_{CO2}), CH_4 and CO yield (Y_{CH4} & Y_{CO}) for catalysts Ru/CeAC **(a)** and Ru/LaCeAC **(b)** versus temperature. Experimental Conditions: 25% H_2, 5% CO_2 in balance with Ar, 1 atm, T (°C): 150-600 °C, F_t = 19 cc/min, m_{cat}= 60 mg.



CH_4 and CO selectivity (S_{CH4} & S_{CO}) for catalysts Ru/CeAC and Ru/LaCeAC versus temperature. Experimental Conditions: 25% H_2, 5% CO_2 in balance with Ar, 1 atm, T (°C): 150-600 °C, F_t = 19 cc/min, m_{cat}= 60 mg.

Conclusions



CO_2 conversion (X_{CO2}), CH_4 yield and selectivity (Y_{CH4} & S_{CH4}) for catalysts Ru/CeAC versus TOS (Time-on-stream, h). Experimental Conditions: 25% H_2, 5% CO_2 in balance with Ar, 1 atm, T (°C): 380 °C, F_t = 19 cc/min, m_{cat}= 60 mg.

The up to 70% CH_4 yield obtained reveals that synthetic Ce-based Aminoclays can be successfully used as supports for the design of efficient CO_2 methanation catalysts.

References

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Acknowledgements

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