

Catalytic performance and stability of Ru nanoparticles supported on novel Ce-based aminoclay for Sabatier reaction.

C. Drosou¹, A. Kaloudi², P. Zygouri², K. Spyrou², D.P. Gournis^{2*}, and I.V. Yentekakis^{1,3*}

¹School of Chemical & Environmental Engineering, Technical University of Crete, Chania, Greece/European University on Responsible Consumption and Production (EURECA-PRO); ² Department of Materials Science and Engineering, University of Ioannina, Ioannina, Greece; ³ Institute of GeoEnergy, Foundation for Research and Technology-Hellas (FORTH/IG), Chania, GR.

* To whom correspondence should be addressed: dgourni@uoi.gr and igentekakis@tuc.gr.

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1. Introduction

The catalytic hydrogenation of CO₂ to produce CH₄, also known as CO₂ methanation or Sabatier reaction ($\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$; $\Delta H^\circ = -164.7 \text{ kJ/mol}$) is considered an extremely important route for CO₂ recycling [1,2]. The reaction is exothermic, thermodynamically favored at low temperatures (ca. 200-400 °C), however, kinetically controlled (limited) at this region. Therefore, the development of high-performance CO₂ methanation catalysts is a major challenge. Among various metals, Ni and Ru are among the most active Sabatier catalysts and have been extensively studied in an attempt to further promote their activity through metal-support interactions or other promotion strategies [1,2].

Due to their unique combination of swelling, intercalation, and ion exchange properties [3] synthetic Aminoclay analogues (AC) have been employed in many application fields including catalysis, separation, gas adsorption, nanocomposites, ferrofluids, biomedicine and many others [4]. These tailor-made synthetic materials are layered magnesium organosilicates with structure analogous to 2:1 natural phyllosilicate smectite clays with covalently linked organosilicates in place of inorganic silicates, with an approximate composition $\text{R}_8\text{Si}_8\text{Mg}_6\text{O}_{16}(\text{OH})_4$ (R is an organic functionality) [5].

In this study, cerium and lanthanum-cerium synthetic aminoclay analogues with an approximate composition $\text{R}_8\text{Si}_8\text{M}_6\text{O}_{16}(\text{OH})_4$, where R represents propylamine functionalities ($\text{R} = -\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$), and M the cerium and cerium/lanthanum (1:1) metals were successfully prepared, using a facile and effective sol-gel approach. These amine functionalities on the surface of the layers can be protonated in the presence of water, which leads to exfoliation of the layered structure [3,5]. Then, using these Ce-based synthetic Aminoclay (AC) analogues as supports of Ru nanoparticles, the performance of this new class of catalysts was investigated under CO₂ hydrogenation conditions and were found to be highly active and selective towards CH₄ production.

2. Experimental

2.1. Catalysts preparation

Preparation of La-CeAC and CeAC synthetic aminoclay supports: For the preparation of lanthanum-cerium synthetic aminoclay (**LaCeAC**), 1.81 mmol of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and 1.81 mmol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 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 ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$).

Preparation of Ru/Ce-based AC catalysts: Ruthenium was incorporated on Ce-based aminoclay supports using the conventional wet impregnation method.

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Appropriate amounts of Ce-based aminoclay were impregnated by specific volume of a Ruthenium (III) nitrosyl nitrate solution ($N_4O_{10}Ru$, 1.5% w/v/ Ru, Alfa Aesar) 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 on a hot plate at $\sim 80^\circ C$. The resulting material was further dried at $110^\circ C$ overnight and then was calcinated at $450^\circ C$ for 1 h. Under this preparation procedure two **Ru/Ce-based AC** catalysts were prepared: **Ru/CeAC** and **Ru/La-CeAC**. For comparison purposes, a traditional 10wt% Ni/CeO₂ catalyst was also prepared.

2.2 Materials Characterization

The XRD patterns of Acs were collected on a D8 Advance Bruker X-ray diffractometer equipped with graphite-monochromatized Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) from 2° to 80° in steps of 0.02° and counting time 2 s/step. FTIR spectra were recorded with a Jasco FT/IR 6200 on samples in the form of KBr pellets containing $\sim 2 \text{ wt\%}$ AC. TGA experiments were obtained with a rate of $5^\circ C/min$ in air using a Perkin-Elmer Pyris-Diamond Thermogravimetric Analyzer.

2.3 Evaluation of catalytic activity and time-on-stream (TOS) stability

Catalytic activity and time-on-stream (TOS) stability of the catalysts were studied using a 3 mm I.D. tubular quartz, fixed-bed reactor, loaded with 60 mg of catalyst. A feed composition of 5% CO₂, 25% H₂ (i.e., H₂/CO₂=5) balanced with Ar at 1 bar, was used with a total flow rate of 19 cm³/min (WGHSV=19,000 mL/g·h). Catalytic performance was conducted in the range of 100–600°C and after catalysts pre-reduction in a flow of 20% H₂/Ar at 400°C for 1 h followed by exposure to the reaction mixture for 1 h at 400°C. Then, the catalysts were cooled at 100°C and their light-off behavior was obtained by increasing the temperature stepwise ($\sim 30^\circ C/step$). TOS stability experiments were performed at 380°C. Reactants and products were analyzed by online gas chromatography (Shimadzu 14 B). CO₂ conversion and CH₄ or CO selectivities were calculated via Eqs. (1)-(3):

$$X_{CO_2} (\%) = 100 * \frac{C_{CH_4}^{out} + C_{CO}^{out}}{C_{CO_2}^{out} + C_{CH_4}^{out} + C_{CO}^{out}} \quad (1), S_{CH_4} (\%) = 100 * \frac{C_{CH_4}^{out}}{C_{CH_4}^{out} + C_{CO}^{out}} \quad (2), S_{CO} (\%) = 100 * \frac{C_{CO}^{out}}{C_{CH_4}^{out} + C_{CO}^{out}} \quad (3)$$

3. Results and Discussion

Fig. 1a shows the XRD patterns of the La-CeAC and CeAC samples. Both diffraction patterns show a strong low-angle peak, below 12° , that is attributed to 001 reflection. The basal spacing of the two clays is estimated at $d_{001}=27 \text{ \AA}$ for the La/CeAC and $d_{001}=8 \text{ \AA}$ for CeAC, respectively, which indicates the thickness of the regularly layered unit clay structure with a bilayer arrangement of propylamino groups [3]. The broad in-plane diffraction peaks at higher angles, $d_{020 \cdot 110} = 3 \text{ \AA}$ and $d_{130 \cdot 200} = 2 \text{ \AA}$, represent the amorphous phase of the synthetic aminoclay analogs confirm the formation of a 2:1 magnesium-phyllosilicate clay with a talc-like structure [3].

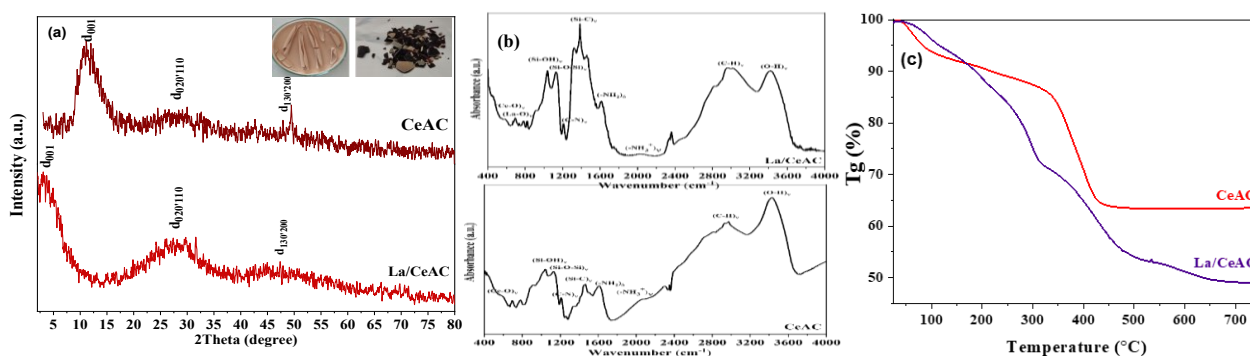


Figure 1. (a) XRD patterns of CeAC and La-CeAC; Inset pictures: Synthetic aminoclay analogues of La-CeAC (right panel) and CeAC (left panel). (b) FTIR spectra of La-CeAC (top) and CeAC (bottom). (c) Thermogravimetric (TGA) measurements of La-CeAC (purple) and CeAC (red).

FTIR spectra (Fig. 1b) show the all the characteristic bending and stretching vibration peaks of the aminoclay skeleton verifying the successful formation of the new synthetic aminoclay analogues. Both spectra show vibrational peaks centered at 3415, 2960, 2030, 1380, 1207, 1130 and 1030 cm^{-1} corresponding to the stretching vibrations of O-H, C-H, $-NH_3^+$, Si-C, C-N, Si-O-Si, and Si-OH respectively, while a band at 1067 cm^{-1} due to bending vibration of $-NH_2$ is detected [6]. Moreover, for

the La-CeAC sample (right panel), the peaks at 583 cm^{-1} and 686 cm^{-1} represent the stretching vibrations of Ce-O [7] and La-O [8], respectively of the La/CeAC aminoclay, while for the CeAC sample (left panel) the peak at 576 cm^{-1} corresponds to the stretching vibration of Ce-O [7]. A two-stage weight loss for both La-CeAC and CeAC samples is observed in thermogravimetric measurements (Fig. 1c). The first stage between $30\text{--}150^\circ\text{C}$ is mainly due to water molecules absorbed on the surface and within the interlayers of the La-CeAC and CeAC structures, verifying the hydrophilic nature of these synthetic clays. The second stage of weight loss between $150\text{--}700^\circ\text{C}$ corresponds to the decomposition of organic compounds present in the ACs. The remaining 48wt% and 65wt% of the La-CeAC and CeAC, respectively, is the inorganic part of the layered materials namely the silicon, cerium, and lanthanum oxides produced upon combustion of the materials.

Figs 2a and b illustrate CO_2 methanation performance (X_{CO_2} , S_{CH_4} and S_{CO}) of Ru/CeAC and Ru/La-CeAC catalysts. As can be seen, both catalysts present high CO_2 conversion, 78% and 75%, respectively, compared to the commonly used Ni/CeO₂ catalyst ($\text{Ru/CeAC} \sim \text{Ru/La-CeAC} \gg \text{Ni/CeO}_2$). Finally, according to the TOS experiment results on the best-performing catalyst, Ru/CeAC, (Fig. 2c), Ru nanoparticles supported on AC offer quite stable CO_2 methanation performance.

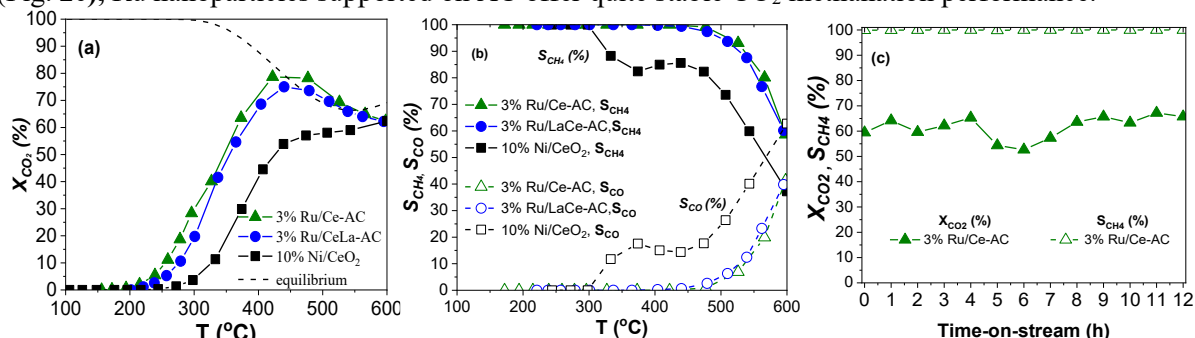


Figure 2. CO_2 conversion (X_{CO_2}) (a), CH_4 and CO selectivity (b), and CO_2 conversion (X_{CO_2}) and CH_4 selectivity (S_{CH_4}) in a twelve hours' time-on-stream stability test at 380°C (c). Feed conditions: 25% H_2 , 5% CO_2 , balance Ar at 1 bar, WGHSV=19,000 $\text{mL/g}\cdot\text{h}$.

4. Conclusions

Ru nanoparticles (3wt%) deposited on novel synthetic aminoclay analogues La-CeAC and CeAC supports exhibit good CO_2 methanation and TOS performance, outperforming that of a traditional 10wt% Ni/CeO₂ catalyst. The up to 80% CH_4 yield obtained reveals that synthetic Ce-based ACs can be successfully used as supports for the design of efficient CO_2 methanation catalysts.

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