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

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Carbon dioxide (CO_2) is a colorless, and odorless greenhouse gas (GHG) with a faint acid taste. It can be found naturally in springwater, etc., while it is the main anthropogenic pollutant from fossil fuel burn. 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.[1]

The catalytic hydrogenation of CO_2 to produce CH_4, also known as CO_2 methanation or Sabatier reaction ($CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$; $\Delta Ho = -164.7$ kJ/mol) is considered an extremely important route for CO_2 recycling. The reaction is exothermic, thermodynamically favored at low temperatures (ca. 200- 400 °C), however, kinetically controlled (limited) at this region. 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.[2,3]

Due to their unique combination of swelling behavior, intercalation, and ion exchange properties, Synthetic AminoClay Analogues (SACA or AC) have been employed in many application fields including catalysis, separation, gas adsorption, nanocomposites, ferrofluids, biomedicine etc.[4–6] 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 $R_8Si_8Mg_6O_{16}(OH)_4$, where R is an organic functionality.[7,8]

In this study, cerium, and lanthanum-cerium synthetic aminoclay analogues with an approximate composition $R_8Si_8M_6O_{16}(OH)_4$, where R represents propylamine functionalities (R = $-CH_2CH_2CH_2NHCH_2CH_2NH_2$), and M the cerium and lanthanum/ cerium (1:1) metals were successfully prepared (CeAC and La-CeAC). The preparation process is a green, facile, and cost-effective room-temperature sol-gel-based synthetic method using metal chloride and aminotrialkoxysilane precursors. Using these cerium and lanthanum/cerium based synthetic Aminoclay analogues as carriers of Ru nanoparticles (Ru/CeAC, Ru/La-CeAC), the performance of this new class of catalysts

was investigated under CO_2 hydrogenation conditions and were found to be highly active and selective towards CH_4 production.

FTIR spectra ensure the successful synthesis of the CeAC and La-CeAC, while XRD patterns confirm the layered structure of the materials (**Figure 1**). As catalytic systems, Ru/CeAC and Ru/La-CeAC exhibit good CO_2 methanation and TOS performance. The up to 80% CH_4 yield obtained reveals that Ru/CeAC can be successfully used as efficient CO_2 methanation catalysts (**Figure 2**).

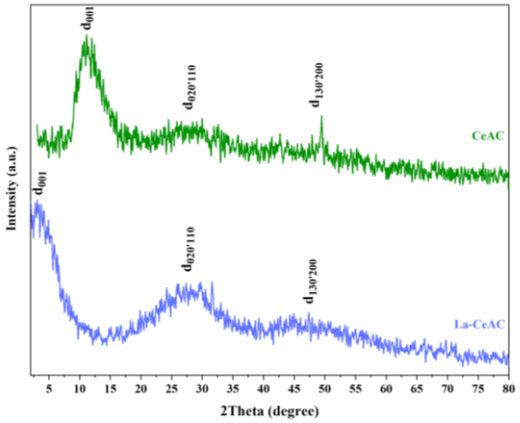

Figure 1. XRD patterns of CeAC and La-CeAC.

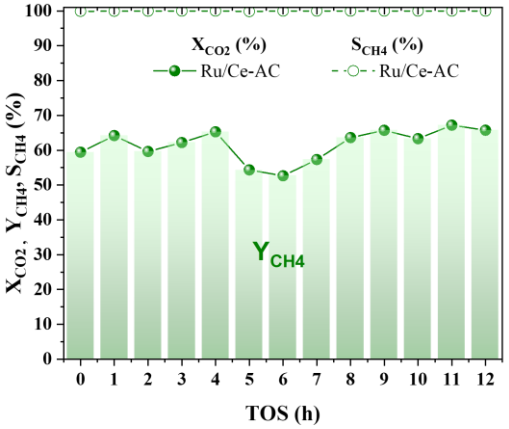

Figure 2. CO_2 conversion (X_{CO2}), CH_4 yield and selectivity (Y_{CH4} & S_{CH4}) for catalysts Ru/Ce-AC versus TOS (Time-on-stream, h). (T= 380ºC).

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