

Study of ceria-based materials for CO₂ capture and their functionalization with ruthenium for methane production

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Introduction

Nowadays, one of the critical challenges of humankind is reaching a carbon-neutral society by 2050, reconverting industrial processes, and reducing greenhouse gas emissions. Carbon capture, and utilization systems (CCUS) are believed to be a hopeful strategy to abate the CO₂ amount produced by industrial flue gas. Moreover, the conversion of this sequestered gaseous waste molecule (CO₂) to value-added chemicals or fuels allows a potential economic profit becoming a feasible alternative to the only costly capturing processes.¹ In this scenario dual-function materials (DFMs) allow the seizure and *in-situ* conversion of a CO₂ feed gas to methane stream gas (synthetic natural gas). In this work, ruthenium-ceria composite materials were developed with the purpose of fulfilling a catalyst with a smaller amount of noble metal and sorbent component keeping it economically competitive and cost-effective. CeO₂ possesses higher activity and selectivity to methane;² ruthenium was selected since it presents optimum chemisorption energy, a great capacity to activate H₂, and an optimum selectivity toward methane formation.³ Firstly, CeO₂ was dispersed onto high surface area materials in order to increase the adsorbent properties of lanthanide oxide dispersed onto two commercial high surface area supports (Al₂O₃ and zeolite ZSM-5). Their adsorption capacities were investigated at three temperature ranges (150°C, 200°C, and 250°C) and, furthermore, exploring their catalytic abilities to convert CO₂ to methane after ruthenium functionalization.

Experimental Methods

Six ceria-base materials with three different concentrations of CeO₂ (10%, 20%, and 30%wt) were dispersed onto aluminum oxide and H-ZSM-5 through an impregnation method. Their adsorption capacities were explored in a laboratory gas-adsorption implant at different temperatures (150, 200, and 250°C) at atmospheric pressure. The most promising materials at 250°C were later functionalized with ruthenium (2 wt%) by adding dropwise a water solution of ruthenium precursor. The catalysts were characterized by several characterization techniques, including XRD, N₂ physisorption at -196 °C, TPDRO, ICP-MS, XPS, FESEM, HRTEM, and FT-IR. Methanation tests were performed as follows: pretreatment in N₂ (150 mL/min, 400°C) and then in 5% H₂/N₂ atmospheres (150 mL/min, 400°C), CO₂ adsorption phase (8% CO₂/N₂, 150 mL/min, 250°C), and a second hydrogenation step (150 mL/min, 250°C) to convert the activated CO₂. The two types of catalysts were tested in repeated runs of cyclic experiments, simulating a continuous use of the material.

Results and Discussion

The adsorption capacities of ceria-base materials were investigated by means of breakthrough curves, considered as reference reactor without the adsorbent (blank). As depicted in **Figure 1A**, an increase in temperature negatively affects the adsorption capacities of material. The CO₂ adsorption uptakes followed this trend for all three temperatures, considering the cerium oxide percentage loading: 10% < 20% < 30%. Moreover, the Al₂O₃-supported materials achieved lower amounts of CO₂ adsorbed than zeolite-supported ones, highlighting the beneficial function of zeolite support played a synergistic role with cerium oxide in the absorption phenomenon. In adsorption experiments, 30% CeO₂/Al₂O₃ and 30% CeO₂/ZSM-5 attained the best results and were selected as composite materials for the subsequent impregnation step to synthesize the ruthenium-loaded catalyst employed in the CO₂ conversion to methane. 2% Ru/30% CeO₂/Al₂O₃ (**Figure 1B**) captured approximately the same

amount of CO₂ in each experiment, from a minimum of 101 μmol g⁻¹ in test 3 to a maximum of 123 μmol g⁻¹ in test 4. The catalytic yields, distinguished by an average value of 90 %, reached his maximum in the first test with 94.9% of CO₂ converted. The bar describing the hydrogen consumption refers to the H₂ used during the catalytic conversion only. Considering the μmol g⁻¹ of methane produced in each test, the amounts of H₂ consumed agreed with the stoichiometry of Sabatier reaction because CH₄ produced followed the 1:4 ratio with hydrogen. On the other hand, 2%Ru/30%CeO₂/ZSM-5 (**Figure 2C**) absorbed on average 35.9% of CO₂ more than Al₂O₃-supported material, achieving a maximum value of 359.2 μmol g⁻¹ in test 2. However, only a small fraction of the adsorbed gas was effectively converted to methane, which exceeded the hundreds of μmol g⁻¹ only in the last test (108 μmol g⁻¹). This behavior could be ascribed to the activity of zeolite support which increased the adsorption capacity of the material together with the CeO₂. It follows that the conversion yields are lesser, reaching the top value in test 5 (32%). The stoichiometric ratio between H₂ and CH₄ produced was kept even in this case.

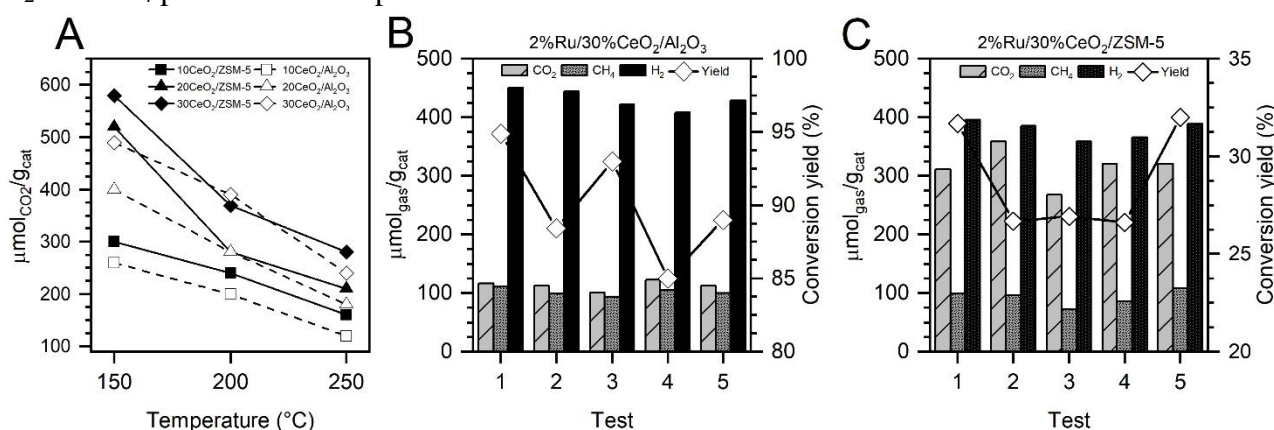


Figure 1: A) CO₂ uptake results from breakthrough experiments, (■,▲,◆) for the zeolite-supported materials, and (□,△,◇) for aluminium oxide-supported ones. B) Results obtained from cyclic methanation experiments carried out on 2%Ru/30%CeO₂/Al₂O₃ and C) those achieved from cyclic methanation experiments carried out on 2%Ru/30%CeO₂/ZSM-5.

Conclusions and future perspectives

The adsorption tests carried out demonstrated that reaching moderate percentage of loaded cerium oxide phase led to a great amount of CO₂ adsorbed at high temperature and the synergic action of zeolite support allowed a further rise in the adsorption capacity. The two ruthenium catalysts were selective to methane production, effective at ambient pressure and at operative temperatures lower than those reported in the literature. Moreover, their performances were stable in repeated tests. These catalysts could be used as promising materials for the application in the simultaneous capture and conversion processes. In that regard, future tasks should focus on improving the relatively lower adsorption capacities of Al₂O₃-supported catalysts, working on the characteristics of adsorbent components. Concerning 2%Ru/30%CeO₂/ZSM-5, the future perspective should concern the valorization of the CO₂ captured, but not converted yet, which could be achieved by modifying the morphology of CeO₂ – leaving the percentage unchanged –, and incrementing the basicity of zeolite support through, for example, an ion-exchange procedure.

References

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