Specific nanostructures of CeO_2 and GDC supports turn iridium to an efficient Power-to-Gas catalyst for the selective hydrogenation of CO_2 to methane.

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Introduction

Thermo-catalytic CO_2 hydrogenation to methane (Sabatier reaction) represents a key pathway for mitigating carbon emissions and enabling renewable hydrogen storage within the Power-to-Gas (P2G) energy model. When coupled with green hydrogen produced via renewable-powered water electrolysis, the process provides a promising route for safe hydrogen storage and transport, overcoming limitations associated with pure hydrogen handling. Depending on the catalyst used, the CO_2 hydrogenation can selectively lead to the formation of methane (CH_4), known as Sabatier reaction: $\mathbf{CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O}$ **(1).** The catalytic performance of CO_2 methanation strongly depends on the nature of the active metal and, critically, on metal–support interactions. Although several non-precious (Ni, Fe, Co) and noble metals (Ru, Rh, Pt) are recognized as efficient methanation catalysts, their activity and selectivity are highly influenced by the support properties and structure.

In the present work, the possibility of transforming iridium —generally considered an inefficient methanation catalyst— into a highly active and selective system was investigated through its dispersion on CeO_2 and GDC ($Ce_{0.9}Gd_{0.1}O_2$) supports with controlled nanostructures.

Materials and methods

CeO_2 and 10 mol% gadolinia-doped ceria (GDC) supports were synthesized via (co-)precipitation and hydrothermal methods, yielding irregularly shaped and nanorod morphologies, respectively. Iridium (2 wt.%) was deposited on CeO_2 and GDC supports using wet impregnation, producing four catalysts: Ir/CeO_2-IRR, Ir/GDC-IRR, Ir/CeO_2-NRs, and Ir/GDC-NRs. A reference catalyst (2 wt.% Ir/γ-Al_2O_3) was also prepared.
Catalytic activity and stability were evaluated in CO_2 hydrogenation (200–600 °C) under fixed feed composition (20% H_2 / 5% CO_2 / 75% Ar) and constant flow rate (Ft = 19 cm^3/min). Comprehensive physicochemical characterization (BET/BJH, SEM, TEM, XRD, H_2-chemisorption, H_2-TPR, and in situ DRIFTS) was performed to correlate catalysts' structural properties with their catalytic performance [1].

Results and discussion

From **Fig. 1**, it is obvious that the reference Ir/γ-Al_2O_3 catalyst exhibited very poor methanation performance, igniting at approximately 400 °C and reaching 50% CO_2 conversion only at around 600 °C. Moreover, its CH_4 selectivity was limited, varying between 45% and 75% within the investigated temperature range. Ir catalysts supported on irregularly shaped CeO_2-based materials (Ir/CeO_2-IRR and Ir/GDC-IRR) showed improved activity compared to the reference catalyst, with lower ignition temperatures (~350 °C) and T_{50} values (~550 °C). However, they produced significantly higher amounts of CO, resulting in relatively lower CH_4 selectivity. In contrast, Ir nanoparticles dispersed on nanorod-shaped CeO_2 and GDC supports exhibited markedly superior catalytic performance. These catalysts demonstrated lower ignition temperatures, enhanced CO_2 conversion, and significantly improved CH_4 selectivity, while suppressing CO formation. The nanorod morphology promotes stronger metal–support interactions, enhanced reducibility, and increased oxygen vacancy concentration, which collectively govern the superior catalytic behavior [1].

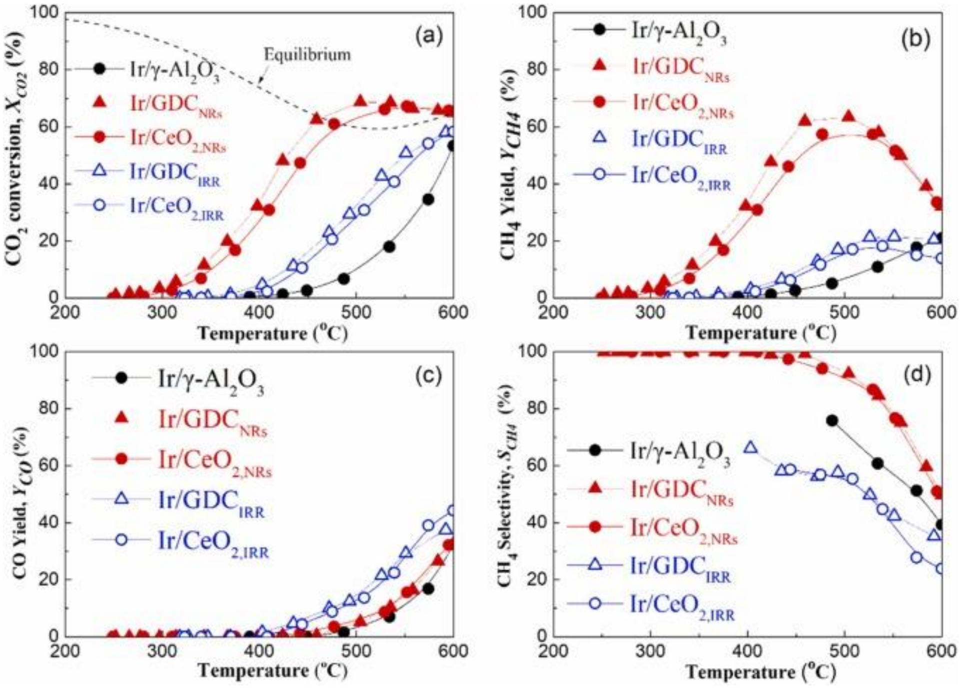

Figure 1. *CO_2 hydrogenation light-off performance of Ir nanoparticles dispersed on ceria-based supports with different nanostructures and on γ-Al_2O_3. (a): CO_2 conversion (X_{CO2}), (b): CH_4 yield (Y_{CH4}), CO yield (Y_{CO}) (c), and corresponding methane selectivity (S_{CH4}) (d) versus temperature. Experimental conditions: 20 % H_2 / 5 % CO_2 / 75 % Ar at 1 bar, catalyst mass m_{cat} = 60 mg, total flow rate F_t = 19.0 cm^3/min, WGHSV = 19,000 cm^3/g·h.*

Conclusions

This study demonstrates that support-shape engineering can dramatically enhance the catalytic performance of iridium in CO_2 methanation. Nanorod-shaped CeO_2 and GDC supports transform iridium from an inefficient into a highly active and selective methanation catalyst. The improved performance is attributed to smaller Ir particle size, stronger metal–support interactions, increased oxygen vacancies, and enhanced reducibility.
These findings highlight support morphology engineering as a powerful strategy for the rational design of advanced metal–oxide nanocomposite catalysts and open new perspectives for shape-induced catalytic promotion [1].

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