

Low-content Ru catalysts for efficient atmospheric CO₂ methanation

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Significance and Relevance

Ruthenium is regarded as a particularly active noble metal in the methanation reaction, exhibiting a low tendency towards deactivation and strong performance even at low loadings $(1\%-5\%)^1$, unlike nickel, which requires a higher loading (~20%). However, the high cost of ruthenium presents challenges to the large-scale development of Ru-based catalysts. Thus, this study aims to investigate the performance of catalysts with ultra-low Ru content (0.25%) during CO₂ methanation at atmospheric pressure. The objectives include comparing supports with varying redox properties to identify the optimal Ru-support combination, thereby maximising activity and stability, and minimising costs in potential industrial applications.

Preferred and 2^{nd} *choice for the topic:* CO₂ utilisation and recycling / sustainable and clean energy production and transport

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The urgent need to reduce atmospheric CO₂, deepened by growing energy demands amid the energy crisis, has intensified research efforts to develop effective strategies for mitigating greenhouse gas emissions while generating value-added products^{2,3}. A promising technology to address these challenges is the power-to-gas (PtG) process, which converts surplus electricity into H₂ via electrolysis, followed by the catalytic methanation of CO₂ in the gas phase⁴. This study investigates low-content Ru catalysts on various supports (Al₂O₃, CeO₂, TiO₂, MgO, ZrO₂), exploring the influence of low Ru loading on catalytic activity and metal-support interactions. Long-term stability tests and CO₂ conversion kinetics studies were conducted to assess catalyst durability and performance.

Materials and Methods

Ru-based catalysts were prepared by employing a water solution of ruthenium (III) nitrosyl nitrate (1.5 % w/w Ru) to impregnate dropwise commercial supports, namely γ -Al₂O₃, CeO₂, TiO₂, MgO, and ZrO₂ samples. These materials were dried at 120 °C for 4 h, calcined at 500 °C for 5 h in air, and reduced with 5 vol% H₂ in N₂ at 350 °C for 40 min. The nominal Ru loading was 0.25 wt% for all the catalysts. Time-on-stream (TOS) tests were conducted with a stoichiometric H₂/CO₂ ratio of 4 at 250 °C for three hours, while activity tests were performed across a temperature range of 200 to 400 °C under the same H₂/CO₂ ratio. Following these initial evaluations, the most effective catalyst was subjected to extended TOS testing (20 - 100 h) to assess its long-term stability and resilience rigorously. This comprehensive approach identified optimal operating conditions and provided insights into the catalyst's sustained performance under realistic process conditions. The morphological and physicochemical properties of the catalysts were thoroughly evaluated using a suite of complementary characterisation techniques, including H₂-TPR, CO₂-TPD, CO chemisorption, N₂ physisorption, XRD, and FESEM.

Results and Discussion

Despite the low Ru loading (0.25% Ru), all the catalysts demonstrated activity for atmospheric methanation, with varying degrees of effectiveness. Catalytic results (**Table 1**) revealed a light-off temperature from 200 to 250 °C under atmospheric pressure for four samples. Ru/TiO₂ exhibited the highest activity, achieving a CO₂ conversion of 21.2% and CH₄ selectivity of 99.8%, with the highest TOF $(1.60 \times 10^{-1} \text{ s}^{-1})$ at 250 °C. These results are likely attributed to strong metal-support interactions, high



catalytic activity of ruthenium species, facilitated by the support's high CO₂ adsorption capacity (186 µmol_{CO2} g⁻¹). Ru/CeO₂ also showed high activity, with a conversion of 11.3% and a comparable TOF of $1.08 \times 10^{-1} \text{ s}^{-1}$, again attributable to a good metal-support interaction (enhanced by ceria's redox properties) and a high catalytic activity of ruthenium species. In contrast, Ru/ZrO₂ and Ru/Al₂O₃ demonstrated lower conversions (7.6% and 6.8%, respectively) and similar TOFs (8.40 \times 10⁻² s⁻¹ and 8.73×10^{-2} s⁻¹), and Ru dispersions of 42% and 35%, respectively. Weaker Ru-support interaction contributed to the lower performance of these two catalysts. Ru/MgO displayed the lowest conversion (0.5%) and TOF (3.46 \times 10⁻³ s⁻¹), despite its high basicity (891 μ mol_{CO₂} g⁻¹). This suggests that the excessive basicity of the support and poor Ru reactivity negatively affected the results of this catalyst. When comparing the performance of the TiO_2 -supported catalyst to that of the conventional Al_2O_3 supported system, Ru/TiO₂ demonstrated a CO₂ conversion threefold higher than that achieved by Ru/Al₂O₃ (21.2% against 6.8%), thereby underscoring its markedly superior catalytic activity. Furthermore, Ru/TiO₂ exhibited a TOF nearly twice that of Ru/Al₂O₃, reflecting a significantly enhanced reactivity of Ru active sites. Both catalysts exhibited high CH₄ selectivity; however, Ru/TiO₂ (99.8%) marginally surpassed Ru/Al_2O_3 (98.8%), indicating the advantageous interplay between the active metal and the TiO₂ support. These findings underscore the importance of balancing support basicity, Ru dispersion and metal-support interaction to optimise catalytic activity for atmospheric methanation.

Table 1. Catalytic performance and main physicochemical properties of the investigated catalysts

Samples	Conversion at 250 °C (%)	Selectivity to CH ₄ (%)	CO ₂ – TPD (μmol _{co2} g ⁻¹)	TOF at 250 °C		SRET
				(s ⁻¹)	%D ⁽¹⁾	(m ₂ g ⁻¹)
0.25% Ru/MgO	0.5	23.0	891	3.46 ×10 ⁻³	18%	99.2
0.25% Ru/Al₂O₃	6.8	98.8	40.6	8.73 ×10 ⁻²	35%	200
0.25% Ru/ZrO₂	7.6	99.0	21.3	8.40 ×10 ⁻²	42%	4.4
0.25% Ru/CeO₂	11.3	96.3	16.4	1.08 ×10 ⁻¹	50%	11.5
0.25% Ru/TiO₂	21.2	99.8	186	1.60 ×10 ⁻¹	59%	45.7

(1) Metal dispersion of Ru particles estimated from selective chemisorption of CO at room temperature. Ru loadings are based on the nominal values.



Figure 1. Morphological images obtained via FESEM microscopy of 0.25% Ru/MgO, 0.25% Ru/TiO₂ and 0.25% Ru/ZrO₂.

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