Design of novel inverse ZrO_2/Ni catalysts for CO_2 utilization: from CO_2 to syn-methane

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Significance and Relevance

The metal-oxide (M-O) interface is crucial in catalysis by guiding the design of highly active catalysts. Unlike conventional catalysts, inverse-phase catalysts load small, inert oxide nanoparticles onto larger, active metal substrates, emphasizing the importance of the O-M interface. In this work, we employed inverse ZrO_2/Ni catalysts for CO_2 methanation, achieving for the first time a unique ZrO_2-Ni interfacial structure. This novel approach led to an enhancement of the catalytic performance and stability of the designed catalyst, providing new insights into interfacial interactions that can improve CO_2 methanation efficiency.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling, Sustainable and clean energy production and transport

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

CO_2 methanation is the most promising and mature route for CO_2 utilization, converting greenhouse gases into valuable fuels and addressing environmental concerns[1]. The catalytic efficiency and stability of Ni-based catalysts in this reaction are influenced by the interaction between metal and oxide phases[2]. In conventional M/O catalysts, the migration of oxides to the surface of the loaded active metal requires high temperatures, resulting in an uncontrollable cover layer, which may make it difficult to distinguish the individual roles of the various O-M interfaces in M/O catalysts[3]. Recent studies suggest that inverse catalysts, where inert oxide nanoparticles are loaded onto active metal surfaces, can enhance catalytic performance by optimizing interfacial properties[4]. This study explores the potential of inverse ZrO_2/Ni catalysts in improving CO_2 methanation efficiency.

Materials and Methods

The inverse ZrO_2/Ni catalysts were synthesized via the impregnation method. A series of characterization methods including BET, XRD, (HR)TEM, H_2-TPR, CO_2-TPD, XPS and *in-situ* DRIFT were carried out to investigate the physicochemical properties of the catalysts.

Results and Discussion

A series of inverse ZrO_2/Ni catalysts with varying Zr/Ni were synthesized and systematically characterized. Figure 1 highlights the catalytic activity results, where the $70ZrO_2$/30Ni catalyst demonstrated exceptional performance, achieving a CO_2 conversion of up to 75% and CH_4 selectivity of 99.7% at 250°C. This catalyst also showed excellent stability, with no observable deactivation over extended reaction times, as illustrated in Figure 2. Comprehensive catalyst characterization revealed that the superior activity of $70ZrO_2$/30Ni is attributed to its larger specific surface area, a higher concentration of medium-strength basic sites, an increased Ni^0 ratio, and a greater concentration of oxygen vacancies, along with enhanced dispersion of ZrO_2 on the NiO support. Additionally, *in situ* DRIFTS analysis confirmed that CO_2 methanation mechanism on these catalysts proceeds via the formate route across all samples. These findings underscore the critical role of metal-oxide interactions in achieving high CO_2 conversion and selectivity, advancing the design of effective inverse catalysts for CO_2 methanation.

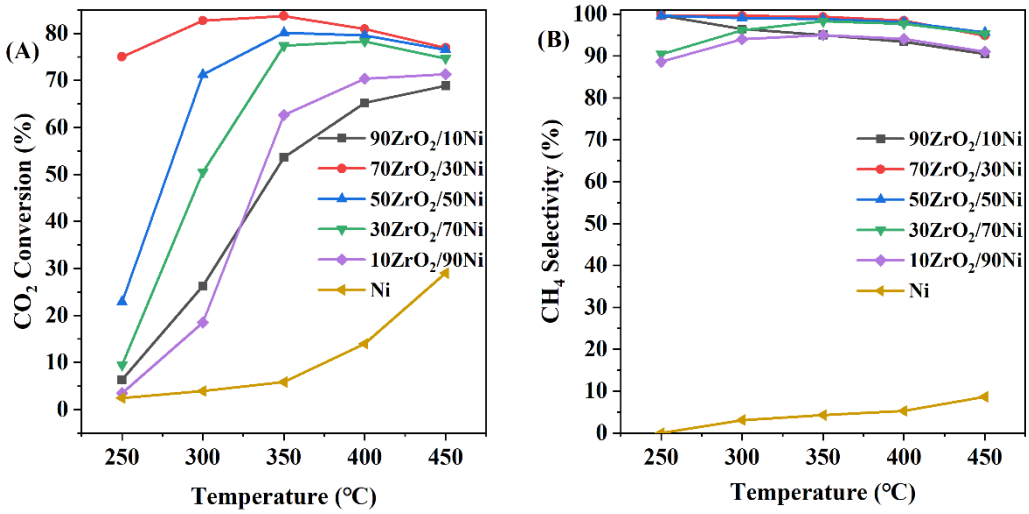

Figure 1 The catalytic activity of different inverse ZrO_2/Ni catalysts (A) CO_2 conversion and (B) CH_4 selectivity (GHSV=30,000 h^{-1}, reduction 1h, 550 ℃)

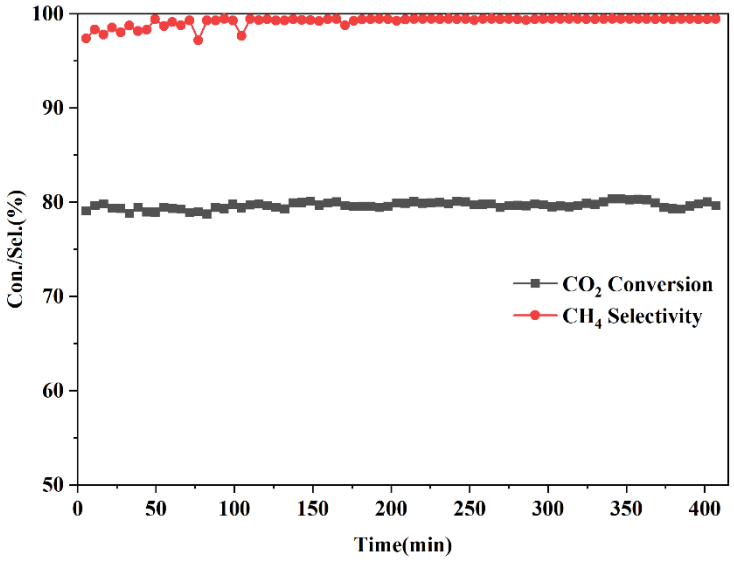

Figure 2 The catalytic stability of 70ZrO_2/30Ni at 300℃ (GHSV=30,000 h^{-1})

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