CO_2 methanation over Ni catalysts supported on CeO_2 and $CeSmO_x$: the influence of adding Sm

Sichen Liu[a], Fabian Rachow[a], Evgenia Charlafti[a], Raquel Sánchez-Barquilla[a], Luisa María Gómez-Sainero[b], Vicente Cortés Corberán[c], Jan Ingo Flege[a]

[a] Fachgebiet Angewandte Physik und Halbleiterspektroskopie, Brandenburgische Technische Universität Cottbus-Senftenberg, K.-Zuse-Straße 1, 03046 Cottbus, Germany
[b] Departamento de Ingeniería Química, Facultad de Ciencias, Universidad Autónoma de Madrid, Calle Francisco Tomás y Valiente 7, Campus de Cantoblanco, 28049 Madrid, Spain
[c] Instituto de Catálisis y Petroleoquímica, CSIC, Calle Marie-Curie 2, 28049 Madrid, Spain

The methanation of CO_2 is an attractive process, which can be operated at mild conditions to obtain CH_4 as a useful synthetic fuel [1]. In comparison to noble metals, Ni as a catalyst seems more appropriate for industrial applications due to its lower price and its high activity [2]. Moreover, the use of CeO_2 as catalytic support has drawn much attention in recent years since it could provide strong metal-support interactions with high dispersion of active centers, and its high basicity could promote the adsorption and activation of CO_2 [2]. Moreover, the addition of Sm_2O_3 into CeO_2 could promote its activity in the methanation of CO_2 [2]. Hence, CeO_2 and Sm-added Ce_2SmO_x are studied as supports of Ni-based catalysts in this work.

The Ce_2SmO_x was prepared through the coprecipitation method with a Ce/Sm atomic proportion of 2:1 using $(NH_4)_2Ce(NO_3)_6$, $Sm(NO_3)_3{\cdot}6H_2O$ and urea as precipitant. Accordingly, a CeO_2 reference sample was prepared by precipitation of $(NH_4)_2Ce(NO_3)_6$. A nickel loading of 20 wt.% Ni was realized by the incipient wetness impregnation method using $Ni(NO_3)_2{\cdot}6H_2O$. The reaction was performed in a continuous fixed-bed tubular reactor employing 0.5 g catalyst at atmospheric pressure with a total flow of 50 ml/min (H_2/CO_2 molar = 4) in 250 ºC – 400 ºC. The products were analyzed through NDIR and FTIR spectrometry. The fresh and used catalysts were analyzed by ICP, BET, XRD, XPS, and TEM.

The experimental results show that the optimal working temperature for both tested catalysts should be 350 ºC, at which a CO_2 conversion of 88% and a CH_4 yield of 80% are reached. When increasing to 400 ºC, the CO_2 conversion begins to decrease in both catalysts, according to the gas-phase equilibrium of the reaction. Interestingly, at the lowest working temperature (250 ºC), the Ni/Ce_2SmO_x shows both higher CO_2 conversion (~ 72%) and CH_4 yield (~ 68%) than Ni/CeO_2 (~ 63% and ~ 55%, respectively). The better performance of Ni/Ce_2SmO_x at low temperature may be attributed to a higher concentration of oxygen vacancies that could promote the adsorption and activation of CO_2, whereas its smaller and better dispersed Ni nanoparticles (14.40 nm Ni/Ce_2SmO_x; 20.84 nm Ni/CeO_2) could also contribute to a higher catalytic activity [2].

Keywords: CO_2, methanation, CeO_2, Ce_2SmO_x, coprecipitation

References

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Corresponding author: Sichen Liu (sichen.liu@b-tu.de)