Tuning oxygen vacant sites and basicity of Ni based catalyst supported on graphene and their effect towards for CO_2 methanation

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CO_2 methanation (**$CO_{2(g)} + 4H_{2(g)} \rightarrow CH_{4(g)} + 2H_2O_{(g)}$, ΔH_{289K}=-165 kJ/mol**) is an exothermic process that can be utilized to mitigate CO_2 emissions and tackle the catastrophic effects of global warming, whilst meeting the growing energy demands. Additionally, methane has higher volumetric energy content than H_2 and less hazardous. Hence, introducing the concept of Power to Gas (PtG) by hydrogenating CO_2 by using the H_2 produced minimizes the hazards associated with H_2 storage [1].

Ni-based catalysts have an exceptional methane selectivity and economic feasibility. However, the low-temperature reaction conditions of CO_2 methanation restricts the catalytic activity of Ni-based catalysts. Optimizing the preparation method of the catalysts to reduce the Ni particle size or to adjust the chemical state of the nickel species can enhance the catalytic performance of Ni-based catalysts during CO_2 methanation. Graphene is a 2D carbon material with advantageous intrinsic properties such as high thermal and chemical stability, and can promote CO_2 activation on the surface of the catalyst. Doped ceria (CeO_2) is known for its oxygen storage capacity (OSC) and redox property [1], which can enhance the performance and coke resistance of the catalyst. Whereas, improving the basicity of the surface of the catalyst by adding a basic metal oxide like MgO, is known to reduce the carbon formed during the reaction.

In this study, the performance of graphene-based supports promoted with 20wt.% MgO (via wetness impregnation) and CePrO (via coprecipitation) metal oxides then decorated with 10 wt.% Ni by wetness impregnation towards CO_2 methanation. Namely, the commercial grade 3 graphene (GR3) produced by LOOP 10 unit (Levidian plasma) and Nanografen (GRP); which is synthesized via pyrolysis. Moreover, a reference 10 wt.% Ni/GR3 catalyst was synthesized via wetness impregnation. XRD and Raman confirmed the formation of cubic fluorite phase CeO_2 in the case of 10% Ni/ CePrO-GR3 and 10% Ni/ CePrO-GRP. NiO peaks have also been detected in all XRD patterns collected. H_2-TPR and CO_2-TPD were utilized to investigate the reducibility and basicity of the catalysts, respectively. The catalytic performance of the catalysts towards CO_2 methanation (CO_2:H_2=1:4 and WHSV=25,000 h^{-1}) was evaluated as a function of temperature (T= 250 ˚C, 300 ˚C, 350 ˚C). The 10% Ni/ CePrO-GR3 catalyst showed exceptional CO_2 conversion as well as selectivity compared to the other carbon-based catalysts used for CO_2 methanation reaction. Whereas, the poor graphene structure of 10% Ni/ CePrO-GRP and the high level of impurities in the pyrolysis type of graphene (e.g. Fe, Si) as those identified in the GRP graphene-like material (SEM/EDX results). Graphene has the ability to donate electrons [1], which is believed to enhance the metal-support interaction which prevents sintering and stabilizes the catalyst and thus prevents its deactivation. The stability tests performed on the catalysts showed that 10% Ni/ CePrO-GR3 maintained the c.a. 93% CO_2 conversion and no CO produced (excellent selectivity) throughout the 100h.

References

[1] M. Mihet, M. Dan, M. D. Lazar, *27* Molecules (2022) 3367.