Ni nanoparticles decorated over Y^{3+} promoted CeO_2 single-atom catalysts for enhanced low-temperature CO_2 methanation

Neha CHOUDHARY[1], Navdeep SRIVASTAVA[2], Biplab GHOSH[3], Patrick DA COSTA[*1]

[1]Institut Jean Le Rond D'Alembert, Sorbonne Université, CNRS UMR 7190, 2 Place de la Gare de Ceinture, 78210 Saint-Cyr-L'Ecole, France
[2]Department of Chemistry, Indian Institute of Technology-Indore, Simrol, Khandwa Road, 433552, India
[3]BARC Beamlines Section, Indus-2, RRCAT, Indore, 452013 India
*patrick.da_costa@upmc.fr

Significance and Relevance

In this work, Ni nanoparticles decorated over Y^{3+} doped over CeO_2 support Single-atom catalysts were prepared to enhance the catalytic activity and selectivity of typical Ni/CeO_2 catalysts. The XPS spectra confirm that the doping of Y^{3+} increases the oxygen vacancies over CeO_2 and consequently enhances the catalytic activity at low reaction temperatures. For comparison, impregnated NiY/CeO_2 and Ni/CeO_2 catalysts were also tested for methanation, which showed less selectivity towards methane products. Moreover, STEM-EDS analysis confirmed the uniform dispersion of Yttrium over CeO_2 in synthesized SACs. The results demonstrate the synergistic effect of Ni with Y to enhance the active sites over CeO_2 support for enhanced catalytic performance.

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Introduction and Motivations

The hydrogenation of CO_2 into CH_4 is an efficient approach for addressing environmental issues related to CO_2.[1] The methanation of CO_2 is receiving increasing focus because of its growing relevance in applications like the power-to-gas concept and long-duration space exploration missions. In this context, catalysts play a crucial role in improving the selectivity towards methane, particularly at low reaction temperatures, and for this purpose, Ni-based catalysts are proven to be good catalysts owing to their low cost. However, Ni/CeO_2 has been extensively explored for the methanation reaction owing to the synergistic effect between Ni and CeO_2 support due to its high surface area and great oxygen mobility. Recently, Cr^{3+} and Eu^{3+} doping over Ni/CeO_2 was reported to generate surface oxygen vacancy over ceria support by creating more $Ce^{3+,}$ consequently enhancing the catalytic performance.[2,3] Moreover, Zhang et al.[4] the dual-active-site SACs were explored where Ru SACs over CeO_2 were prepared with Ni nanoparticles boosted catalytic performance for CO_2 methanation. SACs have high exposure to active sites and enhanced shows both properties of homogeneous and heterogeneous catalysts.[5] On the other hand, the effect of Y over Ni-based catalysts for CO_2 methanation was well-explored by our group, where Yttrium improved the basicity of catalysts and led to stabilizing the catalyst for carbon formation.[6,7] Hence, keeping this in mind, we synthesized Y/CeO_2 SACs with ~5 wt% of Y loading and then Ni nanoparticles were impregnated over as synthesized SACs and named as NiY/CeO_2. Furthermore, for comparison, impregnated NiY NPs over CeO_2 and Ni/CeO_2 were also prepared and tested for methanation reaction. All these catalysts are well-characterized and analyzed for CO_2 methanation reaction.

Results and Discussion

Y/CeO_2 SACs with 1:9 molar ratio was synthesized via co-precipitation method and further Ni nanoparticles were impregnated over as prepared Y/CeO_2 SACs via incipient wetness impregnation method. For comparison, Ni and Y together impregnated over ceria support were prepared by the impregnation method and named as Ni/CeO_2-imp. Additionally, Ni/CeO_2-imp was also prepared without using Yttrium salt. These prepared catalysts were characterized via various characterizing techniques like PXRD, H_2-TPR, CO_2-TPD, H_2-TPD, BET, HR-TEM, STEM-EDS, XPS, EXAFS, ICP-OES etc. PXRD analysis of fresh catalysts confirmed the doping of Y over ceria while shifting of (111) plane of ceria was observed to higher 2θ value, which may be because of the change in interplanar spacing in ceria lattice after doping of Y^{3+} in case of NiY/CeO_2 SACs. Furthermore, the presence of NiO was confirmed through PXRD matches with JCPDS#96-900-8694. N_2 adsorption-desorption analysis confirmed the high surface area and CO_2 TPD showed high basicity in comparison to Ni/CeO_2 catalyst. Furthermore, STEM-EDS analysis was performed, which showed uniform dispersion of Y over ceria even after impregnation of Ni NPs. ICP-OES analysis is in good agreement with the wt% obtained via STEM-EDS analysis where Y is ~5 wt% and Ni is ~7 wt% observed over ceria support. XPS analysis confirmed that NiY/CeO_2 SACs have more surface oxygen vacancies than Ni/CeO_2-imp catalysts, confirming the effect of Y doping over ceria support. Also, XPS spectra revealed higher Ce^{3+} in the case of NiY/CeO_2 than Ni/CeO_2 catalysts. After careful characterization, the set of all catalysts was utilized for the CO_2 methanation reaction, where NiY/CeO_2 showed superior catalytic activity with 82% conversion and ~100% selectivity over undoped Ni/CeO_2-imp and NiY/CeO_2-imp catalysts at 350℃ (**Figure 1**). Moreover, a long test run was also performed to utilize the robustness of the NiY/CeO_2 SAC for 40 hours, which showed no significant change in catalytic performance. These results provide a valuable perspective for assessing the hydrogenation process, thereby establishing a link between structure and activity performance. Additionally, the results offer important insights into the role of oxygen vacancies and their impact on catalytic activity.[6]

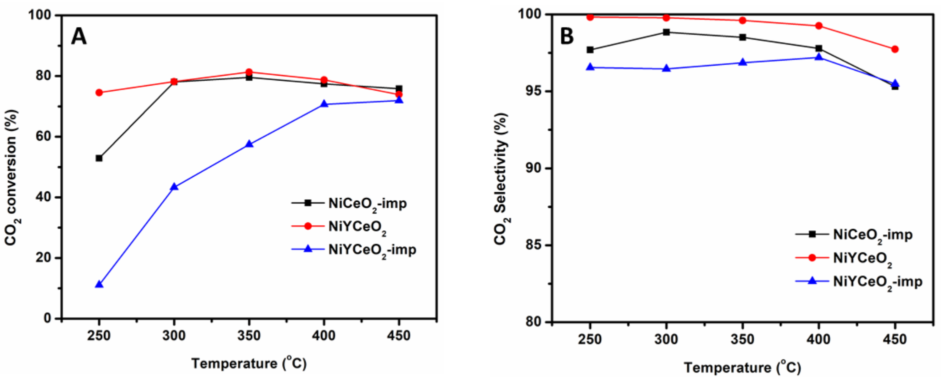

Figure 1. Methanation results of CO_2 methanation with NiY/CeO_2 catalysts (A) conversion and (B) selectivity.

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