Confined growth of ultrasmall NiO nanoparticles into mesostructured and mesoporous SiO_2, γ-Al_2O_3 and CeO_2 supports for CO_2 methanation

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Significance and Relevance

Different NiO- and NiO/CeO_2-based composite catalysts for CO_2 methanation were first obtained by dispersing the active phase into the pores of mesostructured SiO_2 (SBA-15). Particularly, two different impregnation methods, never applied to methanation catalysts to the best of our knowledge, were used, leading to catalysts with a different dispersion of NiO nanoparticles, featuring different catalytic activity. The presence of CeO_2 showed a significant promoting activity and, in this context, different Ni/Ce ratios were studied. Furthermore, other chemically different mesostructured/mesoporous supports (i.e. Al_2O_3 and CeO_2) were studied.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling (preferred); Circular economy (second choice)
Preferred presentation: Oral preferred, Short Oral as second choice

Introduction and Motivations

Due to the increasing attention toward global warming, current research is focusing on green fuels obtained by the reduction of captured CO_2 (e-fuels) with hydrogen obtained from renewable energy sources (green hydrogen). A prominent example of these e-fuels is methane, that is obtained from CO_2 through a reduction reaction called the "Sabatier reaction". Ni-based catalysts are currently among the most investigated systems for CO_2 methanation, due to their high activity and selectivity at relatively low temperatures and due to their low cost compared to catalysts based on noble metals [1,2]. Ni is often paired with a support/promoter, like CeO_2 or Al_2O_3. In this work, composite catalysts consisting of a NiO and NiO/CeO_2 active phase dispersed on mesostructured silica (SBA-15), mesostructured γ-Al_2O_3, and mesoporous CeO_2 are presented. The use of mesoporous/mesostructured supports should allow to obtain a high dispersion of NiO in form of small nanoparticles, leading to a good catalytic activity with a reduced amount of active phase. Chemically different supports have also been studied to determine their effect of the catalytic performance of the catalysts.

Materials and Methods

To obtain NiO- and NiO/CeO_2-based nanocomposites two different impregnation approaches were used: a two-solvent (TS) impregnation and an impregnation based on a self-combustion (SC) reaction. SBA-15 was used as support. NiO-based catalysts (NiO@SBA-15) were obtained with a weight loading of 4.5%; NiO/CeO_2-based ones (NiO/CeO_2@SBA-15) were obtained with the same NiO loading, using a 1:1 Ni:Ce molar ratio (total weight loading = 15%). The total weight loading of 15% was then maintained to study different Ni/Ce molar ratios, ranging from 1/1 to 4/1. To rule out any possible activity of CeO_2, CeO_2-based catalysts were synthesized with a CeO_2 loading of 10.5%. Mesostructured γ-Al_2O_3 and mesoporous CeO_2 were subsequently used as supports to host NiO with a weight loading of 4.5%. To determine their structural, textural, and morphological properties, the catalysts were characterized with both small-angle (SA-) and wide-angle (WA-) XRD (X-ray diffraction), TEM (transmission electron microscopy), and nitrogen physisorption; they were also characterized with TPR (temperature-programmed reduction) and tested for CO_2 methanation.

Results and Discussion

WA-XRD show that the composites obtained with the SC impregnation do not feature any diffraction peak, suggesting that NiO and CeO_2 are deposited into the mesopores as ultra-small nanoparticles. On the other hand, the composites obtained with the TS impregnation show broad but visible crystal reflections attributed to both NiO and CeO_2, indicating that the active phase has crystallized forming larger nanoparticles. This finding is also confirmed by TEM micrographs, which, for SC composites, do not show the presence of any visible particle attributable to the active phase outside the mesopores; TS systems, conversely, visibly show darker nanoparticles dispersed over the support.

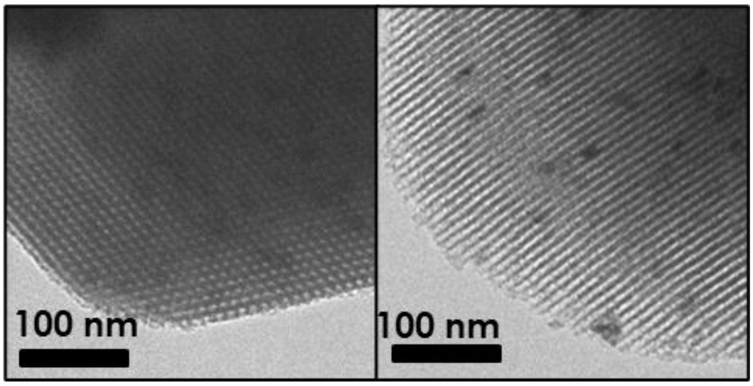

Figure 1 TEM micrographs of two NiO/CeO_2@SBA-15 composites obtained with SC (left) and TS impregnation (right).

The catalytic tests show a significantly positive effect of CeO_2 as promoter on performances in terms of CO_2 conversion (X CO_2 = 19% for NiO@SBA-15_SC vs. 48% for NiO/CeO_2@SBA-15_SC); furthermore, the catalysts obtained with the SC impregnation show a higher CO_2 conversion (X CO_2 = 48% for NiO/CeO_2@SBA-15_SC vs. 38% for NiO/CeO_2@SBA-15_TS), presumably due to the higher dispersion of active phase obtained with this approach. The Ni/Ce ratio, studied on 15 wt% composites obtained with the SC method, also shows a remarkable effect on the performance, with the 2/1 ratio featuring better performances than the 1:1 ratio. The effect of the different support (mesostructured γ-Al_2O_3 and mesoporous CeO_2) on the catalytic behavior, was also investigated.

References

1. W.J. Lee, *et al*. *Catalysis Today,* **2021**, 368, 2-19.
2. M.A.A. Aziz *et al*. *Green Chemistry,* **2015**, 17, 2647-2663.

Acknowledgements

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