Liquid-Assisted Grinding as an alternative synthesis method of NiO/MCM-41

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Highlights

- Preparation of the MCM-41 supported NiO by using liquid-assisted grinding method.
- Comparison of the physico-chemical properties of the samples, obtained by ball-milling to the samples, prepared by *in situ* wet impregnation
- Potential utilization of the prepared materials in plasma-catalytic ammonia production.

1. Introduction

Mesoporous Silica Nanoparticles (MSNs) have been widely researched due to their porosity, high specific surface areas and robust chemical composition, which makes them an interesting material for various applications, such as water treatment, drug delivery systems, energy storage and catalysis.[1] Wang *et al.*[2] identified Ni/MCM-41, with the mean particle size of 15 nm, as a promising catalyst for plasma-catalytic production of ammonia, which have been widely researched as a possible alternative to Haber-Bosch synthesis. The size of metal active sites significantly effects the efficiency of plasma-catalytic ammonia production. Gorky *et al.*[3] reported, that the reduction of Ni sites from 13.5 nm to 5.6 nm increases the energy yield of the reaction system by 90%. In the pursuit of finding a more efficient catalyst for plasma-catalytic ammonia production we explored liquid-assisted grinding method for the synthesis of nickel oxide catalyst supported on MCM-41, which reduced the particle size and enabled a homogenous dispersion of NiO on the surface.

2. Methods

The MCM-41 support was prepared by following the procedure from the literature.[2] For liquid-assisted grinding method the nickel precursor, MCM-41 and deionized water were added to the 50 mL stainless steel ball milling jar along with the stainless steel grinding balls. In order to achieve the optimum conditions, different parameters such as reaction time, frequency, number and size of the grinding balls, as well as the volume of deionized water, were varied. To compare the properties of the obtained products, the same supported materials with comparable metal loadings were prepared by *in situ* wet impregnation.[2] All samples were characterized by using Powder X-Ray Diffraction (PXRD), nitrogen physisorption, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

3. Results and discussion

The PXRD analysis confirmed, that the support kept its ordered porous structure after the impregnation with metal oxides in the ball mill. This was determined based on the presence of intense diffraction peak, ascribed to the (100) at approximately 2.3°. Scanning electron microscopy was used to compare the morphology of the samples. The SEM images of the sample prepared by the *in situ* impregnation method, as well as the sample prepared by liquid-assisted grinding method can be seen in Figure 1. By comparing the images of both methods with comparable NiO loading, it can be observed that the particles, obtained by *in situ* method are significantly smaller, which was expected. Implementing smaller particles may subsequently improve the catalytic activity of the material and therefore yield higher reaction efficiency. During the optimization of the synthesis, a larger individual NiO particles, not deposited on the MCM-41, which indicated an uncomplete impregnation, were seen in the SEM

images. Another indication of the uncomplete impregnation was the change of the nitrogen physisorption isotherm from type IV to type II.

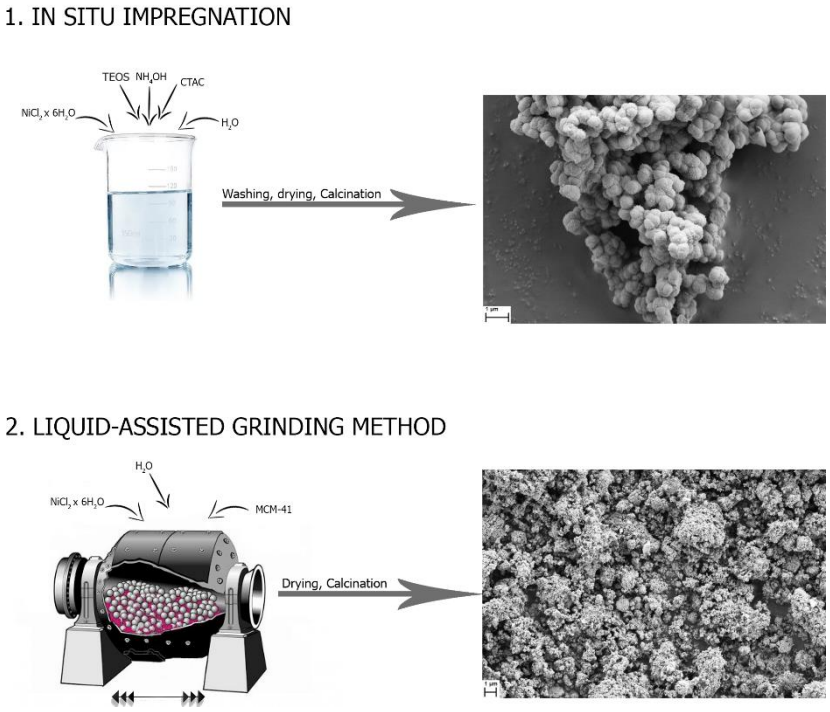

Figure 1. Synthesis methods with SEM images of the products.

4. Conclusions

MCM-41 supported NiO material was successfully obtained by the ball milling method with addition of small amount of solvent. The same material was prepared by the procedure from the literature. The impregnation by liquid-assisted grinding yields significantly smaller particles, which could improve the catalytic activity of the material.

References

[1] R. R. Castillo,L. de la Torre, F. Garcia-Ochoa, M. Ladero, M. Vallet-Regi, Int. J. Mol. Sci. 21 (2020) 7899.
[2] Y. Wang, W. Yang, Xu S., Chen G., Weidenkaff A., Hardacre C., Fan X., Tu X., J. Am. Chem. Soc. 144 (2022) 12020-12031.
[3] F. Gorky, A. Best, J. Jasinski, B. J. Allen, A. C. Alba-Rubio, M. L. Carreon, J. Catal. 393 (2021) 369-380.

Keywords
mesoporous silica; liquid-assisted grinding; particle size