



## Short communication

## A coke-resistant catalyst for the dry reforming of methane based on Ni nanoparticles confined within rice husk-derived mesoporous materials

Luis A. Salazar Hoyos, Betina M. Faroldi, Laura M. Cornaglia\*

*Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE, Universidad Nacional del Litoral, CONICET, Facultad de Ingeniería Química, Santiago del Estero 2829-3000, Santa Fe, Argentina*

## ARTICLE INFO

## Keywords:

Rice husk  
Coke-resistant Ni catalyst  
Dry reforming

## ABSTRACT

Mesoporous MCM-41 materials were obtained using Rice Husk Ashes (RHA) as silica source. Ni-based catalysts were synthesized using two metal incorporation methods, one-pot synthesis combined with microwave heating, and incipient wetness impregnation. Smaller Ni particles were obtained by the former method. The catalyst denominated Ni-MCM had the best performance in the dry reforming of methane reaction at 873 K. High stability was also obtained even after 100 h on stream at 973 K. The mesoporous structure and Ni nanoparticles were not significantly modified, as observed by TEM microscopy. Besides, a very low amount of carbon deposits was detected employing several techniques in the Ni-MCM catalyst used at 973 K.

## 1. Introduction

The production of hydrogen by the dry reforming of methane (DRM) is a promising process due to the global interest in finding new energy sources. Methane and carbon dioxide react to produce synthesis gas with an  $H_2/CO$  ratio  $\leq 1$ , due to the simultaneous occurrence of the reverse water gas shift reaction (RWGS). Collaterally, the DRM reaction can be used as an alternative to prevent the worrying progress of global warming mainly promoted by the emission of greenhouse gases [1,2]. DRM is a highly endothermic reaction and it is usually carried out at temperatures higher than 873 K. The successful application of this process implies a very active, stable and hydrogen selective catalyst. Nickel catalysts have been extensively studied on different supports due to their low cost and high activity for methane reforming reactions [3–5]. However, Ni-based catalysts have the disadvantage of presenting abundant coke formation under operating conditions. At present, different strategies are followed in synthesis methods to avoid the deactivation by the coking and sintering of metal nanoparticles [6–9]. Long-term stability has been reported for Ni/Mg-Al catalysts [10], as well as for Ni promoted catalysts based on different mesoporous materials such as MCM-41 [11], SBA-15 [12], SBA-16 [13] and also KIT-6 supports [14].

A high metal-support interaction or encapsulation process seems to be the best way to obtain dispersed, confined particles and improve metal stability [2,3,6,12–16]. Current research work shows synthesis routes to selective monometallic and bimetallic cluster encapsulation in

zeolites. These materials have been tested in different reactions showing an excellent performance due to monodispersed and stable clusters formed during the synthesis process [17,18]. The one-pot method also produces highly dispersed metal nanoparticles in comparison to conventional impregnation [14,15].

Rice husk ash (RHA) is an industrial waste with high silicon content. In addition to its potential as a low-cost precursor, its use implies an approach to process integration, since this material is mainly obtained after rice husk burning for power generation [19,20]. In turn, RHA silicon could be converted to a variety of porous silica frameworks, which may have applications as sorbents for gases and liquids, and also as supports for metal catalysts [21–24].

This work proposes the use of RHA to obtain a high purity silica precursor. Mesoporous MCM-41 supports and catalysts were synthesized by hydrothermal synthesis. The one-pot method using microwave heating was used to obtain stable Ni nanoparticles within the mesoporous structure. The best Nickel-based catalyst was tested in the DRM reaction during 100 h, showing a high stability with very low amount of carbon deposits. In the literature, several papers have been published on the development of high stable catalysts. However, to the best of our knowledge, a Ni-MCM-41 catalyst derived from rice husk ashes with high stability, very low carbon deposition, and without promoter addition has not yet been reported.

\* Corresponding author.

E-mail address: [lmcornag@fiq.unl.edu.ar](mailto:lmcornag@fiq.unl.edu.ar) (L.M. Cornaglia).<https://doi.org/10.1016/j.catcom.2019.105898>

Received 19 October 2019; Received in revised form 28 November 2019; Accepted 2 December 2019

Available online 03 December 2019

1566-7367/© 2019 Elsevier B.V. All rights reserved.

## 2. Experimental

### 2.1. Silica extraction and material preparation

RHA was obtained by heat-treating the rice husk in a downdraft reactor. A sodium silicate solution was extracted by refluxing RHA in 1.5 M NaOH at 303 K for 24 h, with a liquid/solid ratio = 15 mL/g RHA. The filtrate solution was used as a silica precursor for the synthesis of mesoporous materials using cetyltrimethylammonium bromide (CTABr) as a template. 622 mg of CTABr were dissolved in 14 mL of sodium silicate solution by vigorous magnetic stirring. The pH was adjusted to 10.5 using glacial acetic acid; this solution was kept under stirring at 303 K for 1 h. The molar composition of the solution was  $1\text{SiO}_2:0.3\text{CTABr}:137\text{H}_2\text{O}$ . The gel mixture was treated under microwave irradiation 500 W at 340 K for 5 h. The white precipitate was filtered, thoroughly washed with deionized water until neutralization, and the solid was dried at 353 K for 24 h. Then, the calcination was carried out to remove the template in a muffle furnace at 823 K for 6 h with a heating rate of 1.8 K/min [2]. As a result, the MCM-41 support was obtained.

The Ni catalyst was prepared following a one-pot procedure. For this purpose, a solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in ethanol was added into sodium silicate and surfactant solution under stirring. The pH was adjusted to 10 for the successful incorporation of the active metal. The resulting mixture was treated in a microwave oven, filtered and dried under the same conditions of the previous synthesis. The calcination was carried out in a muffle furnace at 823 K for 6 h with a heating rate of 1 K/min. This catalyst was denominated Ni-MCM. A supported nickel catalyst was prepared by the incipient wetness impregnation method, with 10 wt% loading of nickel. The  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in the required amount of ethanol and added to the MCM support. The solid was dried at 353 K overnight, before being calcined in air flow at 823 K for 6 h with a heating rate of 1 K/min. In this case, the catalyst was denominated Ni/MCM.

### 2.2. Catalyst characterization

The chemical composition analysis was performed by X-ray Fluorescence Spectrometry, by dispersion energy (Model EDX-720, Shimadzu). The surface area of the material was measured by BET analysis (Micromeritics, ASAP 2020) with pretreatment at 473 K for 8 h. X-ray scattering experiments were carried out using a XEUS1.0 equipment. The crystalline structure of the samples was examined by X-Ray Diffraction (XRD) using a ShimadzuXD-D1 equipment. The reducibility of the catalysts was analyzed by Temperature-Programmed Reduction (TPR) using a Micromeritics AutoChemII chemisorption analyzer. Temperature-programmed oxidation (TPO) experiments were performed using a 20%  $\text{O}_2/\text{Ar}$  mixture. The reactor outlet was fed into a methanation reactor coupled with an on-line FID detector. For both temperature-programmed measurements, the heating rate was 10 K/min and the flux was 30 mL/min. The Raman spectra were recorded with a Horiba-Jobin-Yvon spectrometer. The XPS measurements were carried out using a multi-technique system (SPECS) [20]. The samples were reduced in  $\text{H}_2$  at 873 K in a tubular quartz reactor and then, at 673 K during 30 min in the load-lock XPS chamber. Transmission electron microscopy (TEM) images were obtained using a JEOL 2100F electron-gun. The fresh sample was reduced at 873 K for 3 h in a 50%  $\text{H}_2$  stream. Particle size was determined by counting 250 particles, using the equation:

$$dp = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where  $n_i$  is the number of particles of diameter  $d_i$ .

### 2.3. Catalytic test

The dry reforming of methane reaction was carried out at 873 K in a tubular quartz reactor (i.d = 6 mm) packed with 0.04 g of sieved catalyst (particle size of 0.3 mm). The catalysts were reduced at 873 K for 3 h using a heating ramp of 5 K/min in a 50%  $\text{H}_2/\text{Ar}$  flux. After that the reactant mixture with a total flow of 30 mL/min with a  $\text{CO}_2:\text{CH}_4:\text{Ar}$  molar ratio equal to 1:1:1 was fed. Reactants and reaction products were quantified by gas chromatography using a TCD detector. The stability tests were performed at 873 and 973 K.

## 3. Results and discussion

### 3.1. Calcined sample characterization

The synthesized materials were characterized by XRF, SAXRD, XRD, XPS, and TEM. The MCM support chemical composition was mainly  $\text{SiO}_2$  with a purity of 97.6 wt%, the residuary percentage corresponded mainly to  $\text{Al}_2\text{O}_3$  with 2.33% and some traces ( $< 0.07\%$ ) of metals like Ca, Fe, and Mn. The measured nickel content for the one-pot catalyst, Ni-MCM, was 8.8 wt%.

Fig. 1 shows the XRD and SAXRD for calcined materials. The MCM support and the Ni-MCM catalyst exhibit typical small-angle reflections of hexagonal structure reported for MCM-41 mesoporous material. Three low-angle diffraction peaks at  $2\theta$  values of 5–6°, the strong peak corresponding to (100) cell parameter and two small peaks (110) and (200) can be clearly resolved according to the hexagonal unit cell. The (100) diffraction peak becomes broader and less intense in Ni-MCM and it has a slight angle position increase of  $0.14^\circ$ , suggesting the incorporation of nickel into the silica framework [2]. This is also evidenced by the absence of the crystalline phase of nickel oxide in the XRD diffraction pattern within the  $2\theta$  range of  $5\text{--}70^\circ$  in the one-pot sample. The diffractogram indicates very small size NiO crystals while for the sample synthesized by wet impregnation, the XRD pattern shows

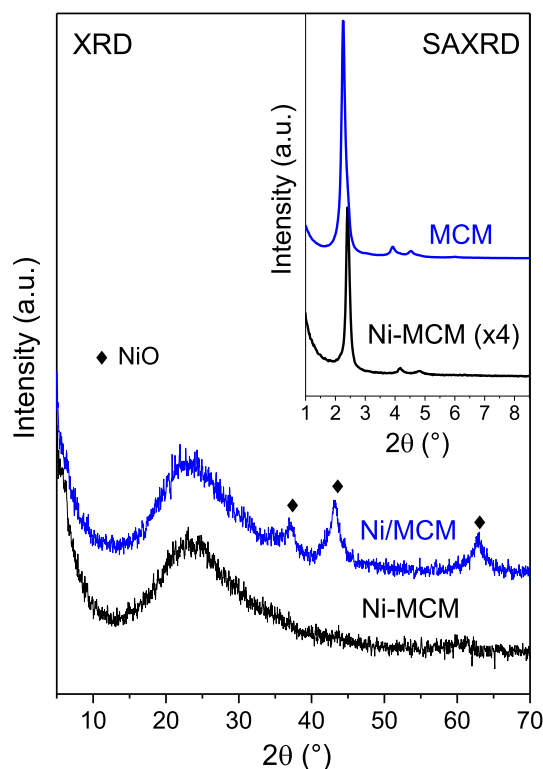


Fig. 1. XRD patterns for the Ni-MCM and Ni/MCM calcined at 823 K; SAXRD for MCM and Ni-MCM ( $2\theta = 1\text{--}9^\circ$ ).

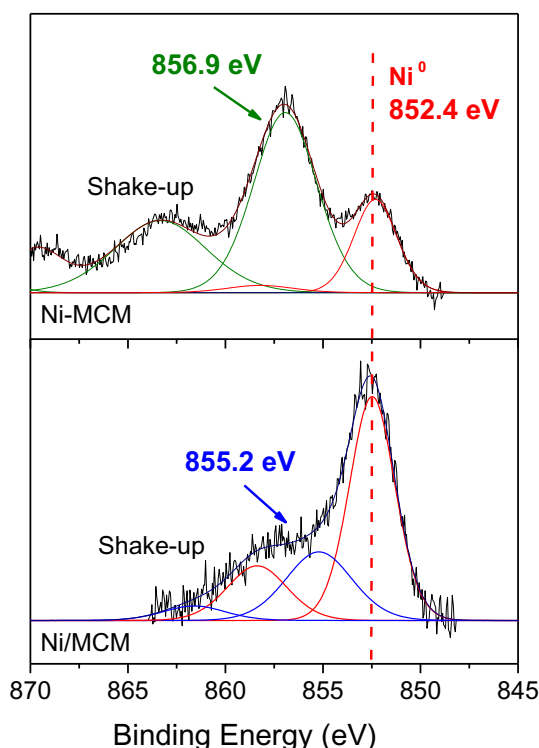


Fig. 2. Ni  $2p_{3/2}$  XPS spectra from reduced Ni-MCM and Ni/MCM catalysts.

the signals corresponding to large nickel oxide crystallites.

The Nitrogen adsorption/desorption isotherms (Fig. S1 in Supplementary Material) of the MCM-41 support and Ni catalysts were classified as type IV according to IUPAC, typical in mesoporous materials. The surface area of the MCM-41 support was  $1067 \text{ m}^2/\text{g}$ ; this value decreased to 789 and  $924 \text{ m}^2/\text{g}$  for Ni/MCM and Ni-MCM catalysts, respectively (Table S1 in Supplementary material).

When the hydrothermal synthesis was performed in a polypropylene flask at  $70^\circ\text{C}$  during 48 h, the MCM-41 mesoporous material was not obtained according with the SAXRD results (not shown). The characterization results show that it was possible to obtain mesoporous MCM-41 structure materials using a silicate solution derived from RHA.

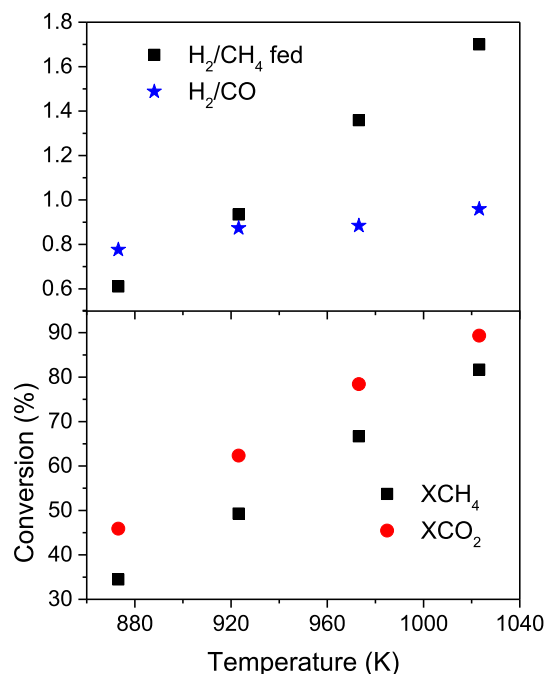


Fig. 4. Catalytic activity of Ni-MCM after reduction at 873 K, at different reaction temperatures.  $W/F = 2.22 \cdot 10^{-5} \text{ g h mL}^{-1}$ .  $\text{CH}_4$  and  $\text{CO}_2$  Conversions,  $\text{H}_2/\text{CO}$  and  $\text{H}_2/\text{CH}_4$  fed values were plotted as a function of the reaction temperature for the Ni-MCM catalyst.

The microwave synthesis allowed obtaining these materials in a shorter time than with the conventional procedure in an autoclave [25].

The TPR profiles (Fig. S2 in the Supplementary material) show the complete reduction of nickel oxide at 950 K for Ni/MCM while for Ni-MCM, a higher temperature was required (1100K). The XPS analysis of the reduced catalysts was carried out in order to study the presence of different surface Ni species. Both samples presented the Si 2 s peak at 154.8 eV and the O 1 s peak centered at 533 eV, corresponding to oxygen on the siliceous support. Fig. 2 shows a significant difference in the Ni  $2p_{3/2}$  spectra; the Ni/MCM mainly exhibited a peak at 852.4 eV associated with reduced Ni species [3] and a smaller contribution at 855.2 eV related with octahedral  $\text{Ni}^{2+}$  clusters. The Ni-MCM sample

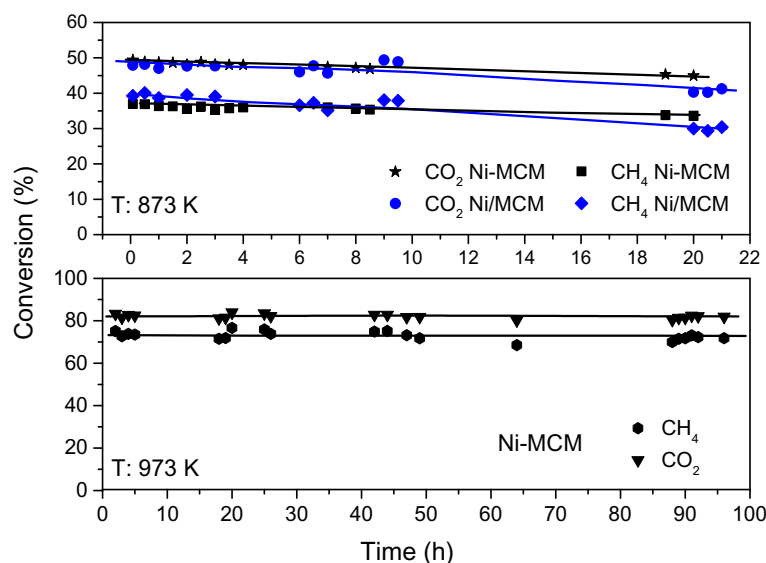


Fig. 3. Stability test of the catalysts after reduction at 873 K in the fixed-bed reactor. (Reaction temperature = 873 K  $W/F = 2.22 \cdot 10^{-5} \text{ g h mL}^{-1}$  and 973 K,  $W/F = 2.57 \cdot 10^{-5} \text{ g h mL}^{-1}$ ). Feed composition:  $P_{\text{CH}_4}:P_{\text{CO}_2}:P_{\text{Ar}} = 1:1:1$ .

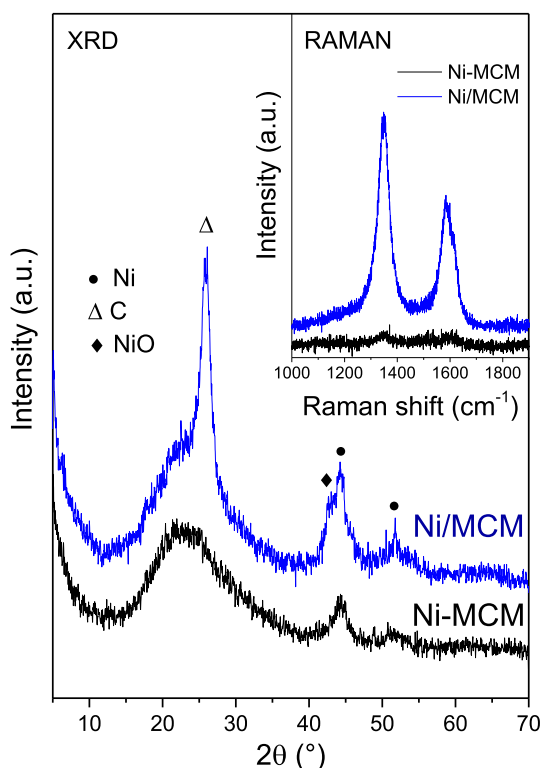


Fig. 5. XRD patterns and Raman spectra of the used Ni-MCM and Ni/MCM catalysts.

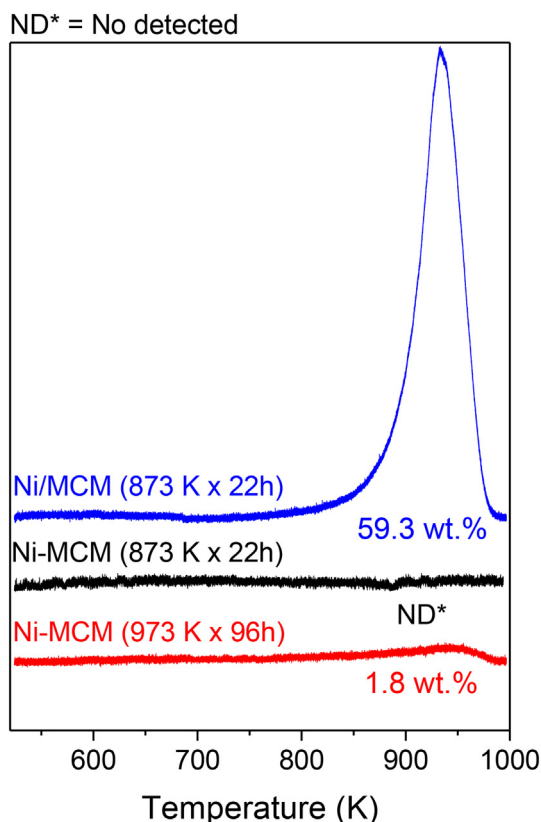


Fig. 6. TPO profiles of the used catalysts.

had a main Ni 2p<sub>3/2</sub> peak at higher binding energies (856.9 eV), assigned to very small Ni<sup>2+</sup> clusters. A low intensity reduced Ni peak was also observed at 852.4 eV.

In both catalysts, a reduced nickel fraction was observed under the treatment conditions carried out prior to the catalytic tests. The Ni<sup>0</sup>/Ni<sup>2+</sup> ratio was higher for the Ni/MCM catalyst.

The XPS analysis showed less reducible Ni species in Ni-MCM than the one obtained by wetness impregnation, indicating a higher interaction with the support.

### 3.2. Catalytic performance

The novel Ni-MCM catalyst synthesized by the one-pot method using RHA as a source of silica was tested on the dry reforming of methane reaction. Fig. 3 shows CH<sub>4</sub> and CO<sub>2</sub> conversion values for the stability test. Thermodynamic calculations predicted an equilibrium conversion value of 41% at 873 K [26]. For both Ni-MCM and Ni/MCM samples, CO<sub>2</sub> conversions were higher than CH<sub>4</sub> conversions, indicating the simultaneous occurrence of the RWGS. The samples showed similar initial conversions; however, the Ni-MCM solid exhibited more stable CH<sub>4</sub> and CO<sub>2</sub> conversion values during 20 h on stream. The H<sub>2</sub>/CO ratio for Ni-MCM was 0.8 confirming the RWGS occurrence. However, the H<sub>2</sub>/CO ratio was 1.1 (Fig. S3) for Ni/MCM, probably due to H<sub>2</sub> and carbon formation through methane decomposition.

DRM is a highly endothermic reaction; therefore, a higher reaction temperature led to higher conversions of methane and carbon dioxide. Fig. 4 shows the reactant conversions as a function of the reaction temperature. As expected, increasing the reaction temperature resulted in higher conversions of CH<sub>4</sub> and CO<sub>2</sub>. In addition, better hydrogen yields (H<sub>2</sub> produced/CH<sub>4</sub> fed ratio) were obtained from 0.6 at 873 K to 1.7 at 1023 K. After that, the catalyst was tested again at 873 K obtaining the same initial performance. It is also important to highlight the stability of the material after being used at 1023 K. At this temperature, the methane and carbon dioxide conversion values were similar because the RWGS reaction was favored to a lesser extent.

A long-term stability test was carried out at 973 K for the one-pot synthesized sample, showing that both conversions were constant during almost 100 h. In previous publications, metal encapsulation has proved to be an interesting route to improve the performance of catalysts [12–18]. In addition, Ni/Mg-Al catalysts with lower Ni loading (2.5 wt%) showed very high stability over > 160 h [10]. In Ni-MCM, the confinement of Ni particles into the mesoporous structure was able to control the carbon deposition leading to a catalyst with very high stability.

The effect of different temperature pretreatments and atmospheres on the catalytic behavior of Ni catalysts supported on MCM-41 was studied by Liu et al. [2]. They observed that materials treated in He compared with those treated in H<sub>2</sub> achieved better yields. During the treatment with He, a small fraction of Ni particles was reduced. However, a short period of exposure to reactants was sufficient to achieve the formation of metallic Ni nanoparticles, particularly active under reaction conditions [2]. A similar behavior could be present in the Ni-MCM catalyst, thus explaining its high activity even though a low proportion of surface metallic species was observed after the reduction treatment. The characterization of the used catalyst could provide more information on the differences on catalytic activities.

### 3.3. Characterization of used catalysts

In the DRM reaction, the lower H/C ratio (H/C = 2) in the reactants favored coke formation and catalyst deactivation, especially in non-noble metals like Ni. The presence of carbon deposits was studied employing XRD, Raman spectroscopy and TPO. Fig. 5 shows the diffractograms and Raman spectra of the used samples. The Ni/MCM solid diffractogram showed a new peak at 2θ = 26° corresponding to graphitic carbon, and also the peaks corresponding to Ni<sup>0</sup> and NiO.



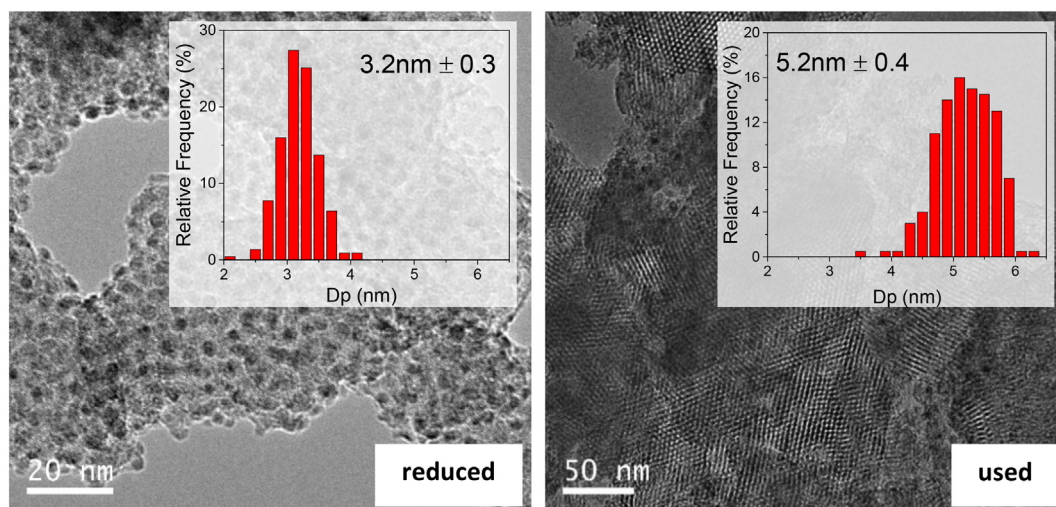


Fig. 7. TEM images of the reduced and used Ni-MCM catalyst; the histograms were included.

However, the Ni-MCM solid diffractogram only showed the  $\text{Ni}^0$  peak.

In the same sense, Raman bands at  $1350$  and  $1600\text{ cm}^{-1}$  confirmed coke formation [13] during the stability test, as was also observed in the TPO profile for the Ni/MCM solid (Fig. 6). However, a low carbon deposition was observed for the one-pot synthesized catalyst even after being on stream during 100 h.

Fig. 7 shows TEM images for the reduced and used Ni-MCM catalyst. In both cases, the MCM-41 structure can be observed, confirming its structural stability. The Ni particles in Ni-MCM had an average size of 3.2 and 5.2 nm for the reduced and used sample, respectively.

All results suggest that One-Pot is a very interesting synthesis method to obtain stable, selective and active Ni nanoparticles in comparison with the impregnation method. A very promising result is that very low carbon deposition was produced during the dry reforming methane test.

#### 4. Conclusions

Mesoporous supports and catalysts were synthesized from rice husk ashes. The materials had appropriate textural properties to be applied in different reactions. The Ni catalysts prepared by one-pot synthesis using microwave heating, showed smaller Ni particles than wetness impregnated catalysts.

The Ni-MCM material was highly stable even after 100 reaction hours at 973 K due to the presence of confined Ni species within the support structure. Additionally, this catalyst exhibited a high structural stability. TEM microscopy showed the MCM-41 typical structure even after being used in reaction. On the other hand, the results of Raman spectroscopy, TPO and XRD did not show carbon deposits after being used at 873 K during 20 h. These properties make Ni-MCM a promising low-cost catalyst to be used in the DRM reaction for hydrogen production.

#### Acknowledgments

The authors wish to acknowledge the financial support received from UNL, CONICET, and ANPCyT and to María Fernanda Mori for the XPS measurements.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2019.105898>.

#### References

- [1] D. Pakhare, J. Spivey, A review of dry ( $\text{CO}_2$ ) reforming of methane over noble metal catalysts, *Chem. Soc. Rev.* 43 (2014) 7813–7837.
- [2] D. Liu, R. Lau, A. Borgna, Y. Yang, Carbon dioxide reforming of methane to synthesis gas over Ni-MCM-41 catalysts, *Appl. Catal. A* 358 (2009) 110–118.
- [3] S. Das, J. Ashok, Z. Bian, N. Dewangan, M.H. Wai, Y. Du, A. Borgna, K. Hidajat, S. Kawi, Silica-ceria sandwiched Ni core-shell catalyst for low temperature dry reforming of biogas: coke resistance and mechanistic insights, *Appl. Catal. B* 230 (2018) 220–236.
- [4] N.A.K. Aramouni, J.G. Touma, B.A. Tarboush, J. Zeaiter, M.N. Ahmad, Catalyst design for dry reforming of methane: analysis review, *Renew. Sust. Energy Rev.* 82 (2018) 2570–2585.
- [5] M. Usman, W.M.A. Wan Daud, H.F. Abbas, Dry reforming of methane: influence of process parameters—a review, *Renew. Sust. Energy Rev.* 45 (2015) 710–744.
- [6] O. Muraza, A. Galadima, A review on coke management during dry reforming of methane, *Int. J. Energy Res.* 39 (2015) 1196–1216.
- [7] E. le Saché, L. Pastor-Pérez, D. Watson, A. Sepúlveda-Escribano, T.R. Reina, Ni stabilised in inorganic complex structures: superior catalysts for chemical  $\text{CO}_2$  recycling via dry reforming of methane, *Appl. Catal. B* 236 (2018) 458–465.
- [8] X. Zhao, H. Li, J. Zhang, L. Shi, D. Zhang, Design and synthesis of  $\text{NiCe@m-SiO}_2$  yolk-shell framework catalysts with improved coke- and sintering-resistance in dry reforming of methane, *Int. J. Hydrog. Energy* 41 (2016) 2447–2456.
- [9] X. Zhao, M. Lu, H. Li, J. Fang, L. Shi, D. Zhang, In situ preparation of Ni nanoparticles in cerium-modified silica aerogels for coking- and sintering-resistant dry reforming of methane, *New J. Chem.* 41 (2017) 4869–4878.
- [10] Q.L. Manh Ha, U. Armbruster, C. Kreyenschulte, H. Atia, H. Lund, H. Thanh Vuong, S. Wohlrab, Stabilization of low nickel content catalysts with lanthanum and by citric acid assisted preparation to suppress deactivation in dry reforming of methane, *Catal. Today* 334 (2019) 203–214.
- [11] A.A. Ibrahim, A.A. Al-Fatesh, H. Atia, A.H. Fakeeha, S.O. Kasim, A.E. Abasaeed, Influence of promoted 5%Ni/MCM-41 catalysts on hydrogen yield in  $\text{CO}_2$  reforming of  $\text{CH}_4$ , *Int. J. Energy Res.* (2018) 1–11.
- [12] Q. Zhang, T. Zhang, Y. Shi, B. Zhao, M. Wang, Q. Liu, J. Wang, K. Long, Y. Duan, P. Ning, A sintering and carbon-resistant Ni-SBA-15 catalyst prepared by solid-state grinding method for dry reforming of methane, *J. CO<sub>2</sub> Utilization* 17 (2017) 10–19.
- [13] S. Zhang, S. Muratsugu, N. Ishiguro, M. Tada, Ceria-doped Ni/SBA-16 catalysts for dry reforming of methane, *ACS Catal.* 3 (2013) 1855–1864.
- [14] Z. Liu, J. Zhou, K. Cao, W. Yang, H. Gao, Y. Wang, H. Li, Highly dispersed nickel loaded on mesoporous silica: one-spot synthesis strategy and high performance as catalysts for methane reforming with carbon dioxide, *Appl. Catal. B* 125 (2012) 324–330.
- [15] X. Xiang, H. Zhao, J. Yang, J. Zhao, L. Yan, H. Song, L. Chou, One-pot synthesis of ordered mesoporous NiSiAl oxides for catalyzing  $\text{CO}_2$  reforming of  $\text{CH}_4$ , *Eur. J. Inorg. Chem.* (2016) 3396–3404.
- [16] C. Wang, X. Jie, Y. Qiu, Y. Zhao, H.A. Al-Megren, S. Alshihri, P.P. Edwards, T. Xiao, The importance of inner cavity space within Ni@SiO<sub>2</sub> nanocapsule catalysts for excellent coking resistance in the high-space-velocity dry reforming of methane, *Appl. Catal. B* 259 (2019) 118019.
- [17] Z. Wu, S. Goel, M. Choi, E. Iglesia, Hydrothermal synthesis of LTA-encapsulated metal clusters and consequences for catalyst stability, reactivity, and selectivity, *J. Catal.* 311 (2014) 458–468.
- [18] T. Otto, S.I. Zones, Y. Hong, E. Iglesia, Synthesis of highly dispersed cobalt oxide clusters encapsulated within LTA zeolites, *J. Catal.* 356 (2017) 173–185.
- [19] G. Sharma, S.K. Ary, K. Singh, Optical and thermal properties of glasses and glass-ceramics derived from agricultural wastes, *Ceram. Int.* 44 (2018) 947–952.
- [20] L. Salazar Hoyos, B. Faroldi, L. Cornaglia, Reactivity of rice husk-derived lithium silicates followed by in situ Raman spectroscopy, *J. Alloys Compd.* 778 (2019)

- 699–711.
- [21] E.-P. Ng, J.-Y. Goh, T.C. Ling, R.R. Mukti, Eco-friendly synthesis for MCM-41 nanoporous materials using the non-reacted reagents in mother liquor, *Nanoscale Res. Lett.* 8 (2013) 120–128.
- [22] Z. Zhang, W. He, J. Zheng, G. Wang, J. Ji, Rice husk ash-derived silica nanofluids: synthesis and stability study, *Nanoscale Res. Lett.* 11 (2016) 502–507.
- [23] S. Pimprom, K. Sriboonkham, P. Dittanet, K. Föttinger, G. Rupprechter, P. Kongkachuichay, Synthesis of copper-nickel/SBA-15 from rice husk ash catalyst for dimethyl carbonate production from methanol and carbon dioxide, *J. Ind. Eng. Chem.* 31 (2015) 156–166.
- [24] R. Vinodh, M. Bhagiyalakshmi, P. Hemalatha, M. Ganesh, M.M. Peng, M. Palanichamy, W.S. Cha, H.T. Jang, Homopiperazine grafted mesoporous silicas from rice husk ash for CO<sub>2</sub> adsorption, *J. Nanosci. Nanotechnol.* 14 (2014) 4639–4648.
- [25] A.N. Rungsi, A. Luengnaruemitchai, S. Wongkasemjit, N. Chollacoop, S.Y. Chen, Y. Yoshimura, Influence of silica sources on structural property and activity of Pd-supported on mesoporous MCM-41 synthesized with an aid of microwave heating for partial hydrogenation of soybean methyl esters, *Appl. Catal. A* 563 (2018) 80–90.
- [26] J. Múnera, B. Faroldi, L. Cornaglia, Nanoparticles in the water–gas shift reaction and steam reforming reactions, in: P. Prinsen, R. Luque (Eds.), *Nanoparticle Design and Characterization for Catalytic Applications in Sustainable*, The Royal Society of Chemistry, 2019, pp. 280–308.