

Supplementary Information

CO₂ reforming of CH₄ over Ni/Mesostructured Silica Nanoparticles (MSN)

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Table S1 Time required for electrolysis and the exact amount of Ni loading onto MSN and MCM-41 as detected by MP-AES and EDX.

Catalysts	^a Time for electrolysis [min]	^b Ni detected in catalyst [%]	^c Ni on the surface [mass %]
Ni/MSN	3.49	1.99	1.91
Ni/MCM-41	3.49	1.98	1.61

^a Calculated time for electrolysis based on Faraday's Law (Eq. 1).

^b The detected Ni presence in the catalyst determined by MP-AES.

^c The detected Ni distributed on the surface of the catalysts obtained from elemental analysis using EDX.

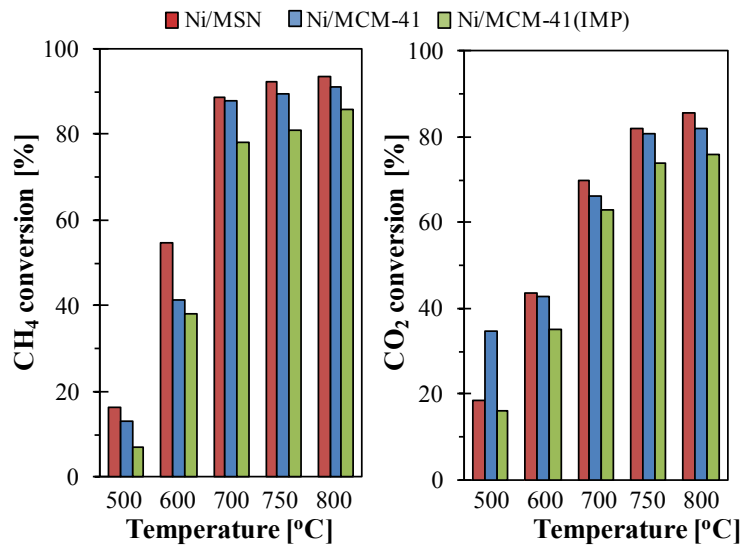


Fig. S1 CH₄ and CO₂ conversions over Ni/MSN, Ni/MCM-41 and Ni/MCM-41 prepared by impregnation catalysts.

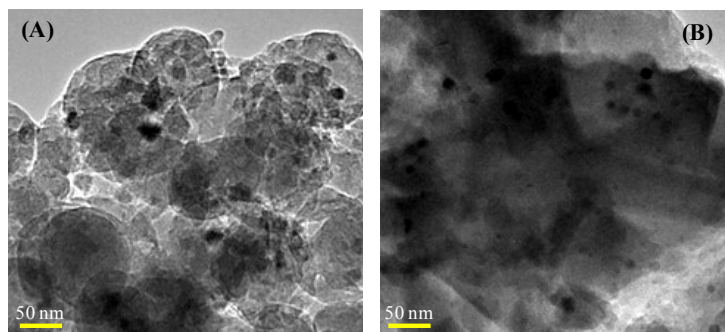


Fig. S2 TEM images of (A) Ni/MSN and (B) Ni/MCM-41 after regeneration 750 °C with 30 min of air and 1 h of H₂

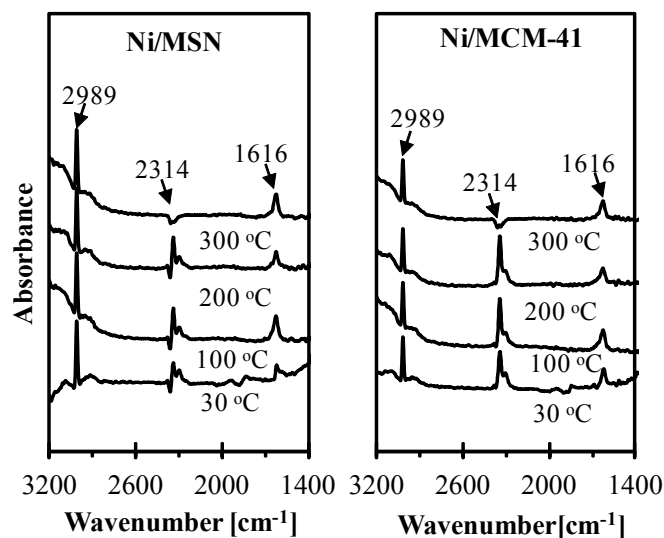


Fig. S3 IR spectra of adsorbed CH₄ and CO₂ on activated Ni/MSN and Ni/MCM-41 when the catalyst were reduced and exposed to 30 Torr of CH₄ and CO₂ at room temperature followed by heating at elevated temperature from room temperature to 300 °C.

Probable mechanism of CO₂ reforming of CH₄ over the Ni/MSN and Ni/MCM-41 was studied using *in-situ* FTIR spectroscopy of adsorbed CH₄ and CO₂ which were recorded after reduction at 400 °C (Fig. S3). When Ni/MSN and Ni/MCM-41 were exposed to 30 Torr of CH₄ and CO₂, intense bands attributable to gaseous CH₄ and CO₂ appeared at 2989 and 2314 cm⁻¹, respectively. In addition, a band at 1616 cm⁻¹ corresponding to adsorbed bicarbonate, was also observed, suggesting the interaction of CO₂ with framework oxygen in the catalysts. Zhang et al. has evidenced that the IR bands of gas-phase CO (at 2170 and 2122 cm⁻¹), which resulted from CO₂ reforming of CH₄ catalyzed by Ni/γ-Al₂O₃ started to appear when the reaction temperature exceeded 400 °C.¹ In another study, Qian et al. observed the presence of CO at the higher temperature of 500 °C over Ni/SBA-15 and La-Ni/SBA-15.² In this study, neither gas-phase nor adsorbed CO bands were detected, because of the limitation of the instrument to perform at higher reaction temperatures (> 300 °C). However, the presence of adsorbed bicarbonate, after exposure to CH₄ and CO₂ at room temperature, suggested the occurrence of strong CO₂ adsorption. Qian et al. only reported the presence of adsorbed bicarbonate for La-Ni/SBA-15, whereas no bicarbonate detection was reported for Ni/SBA-15.² The increasing of temperatures up to 300 °C, the intensities of the above mentioned adsorbed species decreased. However, it is worth mentioning that the signal intensity for adsorbed bicarbonate with the Ni/MSN was relatively higher than that for Ni/MCM-41 at 300 °C, indicating the ability of Ni/MSN to adsorb CO₂ at higher temperatures (as evidenced by the rate of CO₂ conversion for Ni/MSN exceeding Ni/MCM-41; refer Fig. 8). It was, therefore, concluded that the nickel supported on MSN was more active than the MCM-41 in the present study.

1 Z. Zhang, X.E. Verykios, S.M. MacDonald, and S. Affrossman, *J. Phys. Chem.*, 1996, **100**, 744.

2 L. Qian, Z. Ma, Y. Ren, H. Shi, B. Yue, S. Feng, J. Shen, and S. Xie, *Fuel*, 2014, **22**, 47.