Micro- and mesoporous supports for CO_2 methanation catalysts: A comparison between SBA-15, MCM-41 and USY zeolite

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HIGHLIGHTS

- SBA-15 presented similar textural properties whatever the synthesis method used.
- Ni particles were mainly located on the SBA-15 and MCM-41 outer surfaces.
- Ni^0 dispersion was higher on SBA-15 and zeolite materials than on MCM-41.
- The highest TOFs and the lowest NiO band gap was obtained for 15%Ni/MCM-41.
- Improved activity was found when adding Ce due to the enhancement of CO_2 activation.

GRAPHICAL ABSTRACT
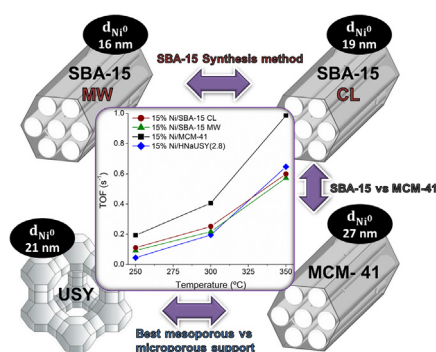
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ABSTRACT

Mesoporous SBA-15 synthesized by two different methods and MCM-41 were used as supports for Ni and Ni-Ce catalysts applied in CO_2 methanation reaction. The performances obtained for both materials were compared taking into account the differences in terms of textural properties, Ni species and reaction mechanism. Results were compared with the reported in the literature for a microporous USY zeolite. XRD, DRS UV–Vis, H_2-TPR and TEM were used for the characterization of the samples. Catalytic tests were performed under the same conditions for all catalysts. Finally, FTIR Operando studies were carried out in order to establish differences from the mechanistically point of view as well as in terms of CO_2 adsorption species for the different samples. Promising data was obtained with the Ni-based SBA-15 catalysts whatever the preparation method. Despite the greater Ni particles size, MCM-41 also reported interesting catalytic performances, so that presenting the highest TOF values among the catalysts studied. The good results obtained for the MCM-41 could be explained by the lower amount of non-reactive carbonyl species adsorbed on the Ni^0 particles surface during the reaction as well as by the enhanced interaction between metal and support reflected in the calculated band gap values. All the results are comparable to the obtained using a HNaUSY zeolite with Si/Al = 2.8 as support. Cerium incorporation on Ni/mesoporous supports allowed enhancing the CO_2 conversion, especially at lower temperatures, as already reported for the zeolite-based samples.

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1. Introduction

CO$_2$ hydrogenation into methane could be an interesting and effective alternative for CO$_2$ emissions mitigation since it is a thermodynamically favourable reaction and methane can be used as fuel in different applications (Centi and Perathoner, 2009; Aresta and Dibenedetto, 2007; Aresta et al., 2013). In terms of catalysts, the most studied metals have been noble metals (mainly Rh and Ru) and transition metals such as Ni. Nickel represents a good alternative to noble metals due to its lower cost and its high catalytic performances (Wei and Jinlong, 2011; Wang et al., 2011). Furthermore, SiO$_2$, Al$_2$O$_3$, CeO$_2$, ZrO$_2$ and Ce/Zr mixed oxides have been deeply investigated as supports for methanation catalysts in the last years (Wei and Jinlong, 2011; Wang et al., 2011). So far, few works have been published dealing with the use of micro and mesoporous materials as supports for Ni-based CO$_2$ and CO methanation catalysts (Graça et al., 2014; Tao et al., 2016; Zhang et al., 2014; Teh et al., 2015; Du et al., 2007; Lu and Kawamoto, 2013; Tao et al., 2016; Zhang et al., 2013; Liu et al., 2015, 2016; Hamid et al., 2017; Bacariza et al., 2015), the mainly used being USY zeolite, SBA-15 and MCM-41. Ni-based USY zeolite catalysts showed interesting performances towards methanation being reported the effect of Ni content, Ce addition, the preparation method conditions and some highlights concerning the reaction mechanism (Graça et al., 2014; Bacariza et al., 2015; Westermann et al., 2015, 2017). In addition, SBA-15 and MCM-41 mesoporous materials were used due to their large pore sizes and interesting textural properties for the dispersion of metal species and the prevention of sintering processes. In addition, SBA-15 is known for the larger pore sizes (4.6–30 nm), higher thermal, mechanical and chemical resistance and higher surface area, when compared to MCM-41 (Nguyen et al., 2008). However, no comparable data was found in the literature for the evaluation of the different micro and mesoporous materials performances in CO$_2$ methanation. As a result, the present work compares Ni catalysts containing the same amount of metal dispersed on two SBA-15 samples synthesized by different methods, a MCM-41 sample and a HNaUSY(2.8) zeolite Graça et al., 2014. The specific activation of nickel, evaluated from TOF determination, and the final dispersion of the metal particles over these materials are also compared. Finally, the effect of Ce incorporation to the Ni-containing mesoporous samples is also studied, in order to confirm the results previously obtained in the literature for zeolite supports (Graça et al., 2014).

2. Experimental

2.1. Catalysts preparation

All samples prepared in the present study are shown in Table 1. In terms of supports synthesis, firstly two SBA-15 supports were prepared following the methods described below. The first one, already reported in the literature (Zhao et al., 1998), was named as classical method (SBA-15 CL) and the synthesis time was of 5 days. This synthesis was performed in acid media using the tri-block copolymer Pluronic 123 (P123, Fluka) as template and tetraethyl orthosilicate (TEOS, Fluka) as silica source. In this way, P123 was dissolved in an aqueous solution of HCl (37%, Sigma Aldich) under stirring at 40 °C and, later, TEOS was added drop by drop. The final solution was kept under stirring during 2 h at 40 °C. After that, a hydrothermal treatment was carried out in an oven at 100 °C for 48 h. Then, the solid was filtered and the template was removed by calcination at 550 °C during 10 h. The second method was a modification of the first one being microwaves heating applied during the hydrothermal treatment, for 2 h at 170 °C (SBA-15 MW) and leading to a synthesis time of two days. Furthermore, MCM-41 was synthesised in alkaline media being cetyltrimethylammonium bromide (C$_{19}$H$_{42}$BrN, Aldrich) used as template and, again, tetraethyl orthosilicate (TEOS, Fluka) as silica source. Firstly, an aqueous solution of C$_{19}$H$_{42}$BrN was prepared at 30 °C being kept under stirring during 15 min. Later, NH$_3$ and TEOS were added keeping the solution under stirring for 1 h. Finally, the solid was filtered and the template was removed by calcination at 550 °C during 10 h.

After synthesis, SBA-15 and MCM-41 supports were impregnated by incipient wetness impregnation method (Graça et al., 2014) with 15%Ni (15%Ni/SBA-15 CL, 15%Ni/SBA-15 MW and 15% Ni/MCM-41) using nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, Sigma-Aldrich, >99%) as precursor salt. For this, a certain mass of support was weighted and an aqueous solution of nickel salt with a water volume close to that of the material pores was added to it drop by drop, being the suspension kept under stirring. After that, samples were dried overnight at 80 °C and, finally, calcined at 500 °C under air flow. Another set of samples containing Ce additionally to Ni was prepared (15%Ce 15%Ni/SBA-15 CL, 15%Ce 15% Ni/SBA-15 MW and 15%Ce 15%Ni/MCM-41). In this case, Ni-samples were prepared as indicated before and, after calcination, Ce was impregnated following the same procedure described above and using cerium acetate sesquihydrate (Ce(C$_2$OOH$_3$)$_3$·1.5H$_2$O, Alfa Aesar, 99.9%) as metal salt. The samples were also dried overnight at 80 °C and calcined at 500 °C under air flow.

In order to compare with microporous materials, two samples with similar metal contents and already reported in the literature (Graça et al., 2014) (15%Ni/HNaUSY(2.8) and 7%Ce 15%Ni/HNaUSY (2.8)) were also presented in this work.

2.2. Catalysts characterization

XRD patterns were obtained in a Bruker AXS Advance D8 diffractometer, using Cu Kα radiation and operating at 40 kV and 40 mA. Two different 2θ ranges were used (0.7–2.5° at a step size of 0.03°/4 s and 5–80° at a step size of 0.03°/2 s) in order to identify the mesoporous structure and the different oxides present in the calcined samples, respectively. XRD patterns of the spent samples were also obtained, in order to analyse the integrity of the materials structure after reaction.

In addition, DRS spectra in the UV–Vis region were obtained in a Varian Cary 5000 UV–Vis–NIR spectrophotometer equipped with a diffuse reflectance accessory in the 200–800 nm range. All reflectance spectra were converted into the Schuster – Kubelka - Munk (SKM) function (F(R)) and presented versus wavelength in order to evaluate the presence of the different Ni and Ce species in the samples.

Furthermore, N$_2$ adsorption measurements were carried out at −196 °C on a Micrometrics ASAP 2010 apparatus in order to obtain the specific surface area, mesoporous and microporous volumes and average pore diameter of the different samples. Prior to the adsorption, samples were degassed under vacuum at 90 °C during 1 h and then at 300 °C for, at least, 4 h.

Table 1
Catalysts studied in the present work.

	Label
Zeolite-based catalysts	15%Ni/HNaUSY (2.8)
	7%Ce15%Ni/HNaUSY (2.8)
SBA-15 based catalysts	15%Ni/SBA-15 CL
	15%Ce15%Ni/SBA-15 CL
	15%Ni/SBA-15 MW
	15%Ce15%Ni/SBA-15 MW
MCM-41 based catalysts	15%Ni/MCM-41
	15%Ce15%Ni/MCM-41