



DBD plasma-assisted CO₂ methanation using zeolite-based catalysts: Structure composition-reactivity approach and effect of Ce as promoter



M.C. Bacariza^{a,1}, M. Biset-Peiró^{b,1}, I. Graça^c, J. Guilera^b, J. Morante^b, J.M. Lopes^a, T. Andreu^{b,*}, C. Henriques^{a,*}

^a CQE - Centro de Química Estrutural, IST - Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisboa, Portugal

^b IREC, Catalonia Institute for Energy Research, Jardins de les Dones de Negre 1, 08930, Sant Adrià de Besòs, Barcelona, Spain

^c Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK

ARTICLE INFO

Keywords:

CO₂ methanation
Plasma catalysis
Zeolites
Structure-reactivity
Nickel-cerium

ABSTRACT

In the present work the effects of the structure composition in terms of Si/Al ratio and Ce addition in the performances of Ni-based zeolites for CO₂ methanation under DBD plasma-assisted catalysis were evaluated. Results were compared with the obtained for a commercial Ni/ γ -Al₂O₃ catalyst and all samples were tested both under thermal and non-thermal DBD plasma conditions. It was found that a higher Si/Al ratio led to better performances not only under thermal but, especially, under plasma conditions, which was attributed to the lower affinity of this sample to water and, thus, to a decrease in the inhibitory role of this compound in Sabatier reaction. Furthermore, the addition of Ce as promoter favoured the dielectric properties of the materials and gave additional sites for CO₂ activation leading to much better results than the obtained for a commercial Ni/ γ -Al₂O₃ sample and for the Ni/zeolite, especially under plasma conditions. Indeed, the best zeolite of this work (NiCe/Zeolite) reported a CH₄ yield of 75% with a power supply of 25 W while, under the same conditions, the commercial sample and the un-promoted Ni/Zeolite presented just 23% and 15%, CH₄ yield, respectively. To our knowledge, this is the first time that a structure-reactivity relationship is attempted with zeolite catalysts under DBD plasma-assisted methanation conditions at atmospheric pressure. These facts also indicate that an important route is being opened, allowing answering to the essential question “what are the important characteristics a catalyst must have to show a better performance under plasma-assisted catalysis?”

1. Introduction

Plasma catalysis is nowadays considered as an emerging branch of plasma processing, being its main features the simultaneous modification of the gas phase composition and the interaction of plasma at the catalyst surface level, allowing synergetic effects promoting a more effective enhancement of the reaction rate [1,2]. Regarding the materials used in plasma processes, different oxides such as CoO_x, MnO_x and TiO₂, carbons, SiO₂, ceria, ceria-zirconia and zeolites have been the most commonly reported [2,3]. Among the different reactions where plasma catalysis has been applied, CO₂ conversion into methane has been gaining attention in the last years, since it could represent a suitable alternative for the large-scale reuse of CO₂ [4–11] together with energy grid stabilisation [12–15]. Ni and Ru-based catalysts with Al₂O₃ as support have been mainly reported [6,7,9,10,16–26], but also a few papers using zeolite-based catalytic systems can be found in the literature [4–6,27].

Regarding the main reported results, Nizio et al. [8] verified that the catalytic performances of Ni/ZrCe systems could be enhanced by the application of non-thermal plasma, especially at lower temperatures. An increase of the CO₂ conversion from 0 to 97% and CH₄ selectivity higher than 90% were observed at ~260 °C, while at higher temperatures (~450 °C) no relevant effects were found. In absence of catalyst and applying plasma, they obtained 5% of CO₂ conversion and only production of CO. In another work [7], the same authors reported similar results for hydrotalcite-based materials containing Ni, Ni-Zr and Ni-ZrCe. In this case, the hydrotalcite-derived material containing only Ni was the one leading to the best performances, while the incorporation of Zr and Ce did not favour the results. Using similar systems, Benrabbah et al. [9] studied the effect of plasma as pre-reduction treatment, being this performed at room temperature in presence of H₂. The catalytic performances were similar to those verified after a conventional thermal pre-reduction. Other study carried out by Zeng and Tu [19] reported the suitability of Cu/ γ -Al₂O₃, Mn/ γ -Al₂O₃ and Cu-Mn/

* Corresponding authors.

E-mail addresses: tandreu@irec.cat (T. Andreu), carlos.henriques@tecnico.ulisboa.pt (C. Henriques).

¹ These authors contributed equally to this work.

γ -Al₂O₃ catalytic systems for CO₂ methanation under plasma conditions at low temperatures. The authors verified that plasma led to an enhancement of the performances in all the cases, being Cu/ γ -Al₂O₃ the catalytic system leading to the highest CH₄ yields.

In the case of zeolite materials, Jwa et al. [4] studied CO and CO₂ methanation in a DBD plasma reactor packed with zeolite pellets impregnated with Ni. According to their studies, CO₂ hydrogenation involves the dissociation of CO₂ into CO and O adsorbed on the active sites of the Ni/zeolite catalysts. Since these dissociated species were suggested to react with hydrogen leading to the formation of methane, plasma could help in the dissociation of the adsorbed molecules, favouring the catalytic performances. In more recent studies, Azzolina-Jury and Thibault-Starzyk [5] proposed a mechanism of CO₂ methanation under glow discharge plasma conditions at low pressure over a Ni/USY zeolite catalyst. Their studies were carried out in a FTIR Operando unit under low pressure, where they verified a CO₂ conversion of 60% with 99% of selectivity to CO in absence of catalyst and under plasma conditions. In addition, they found out that a relatively low amount of CH₄ could be generated in gas phase, but only a proper catalyst could enhance CH₄ selectivity. Even if in the literature the possibility of microdischarges happening inside pores was reported [3], they suggested that this effect could not be relevant in Ni/USY zeolites, since (1) metallic Ni particles acting as active sites were mainly located on the external surface of the zeolite and (2) USY zeolite pores (1 nm range) are considerably much smaller than the studied in the literature (10–100 μ m [3]). The authors proposed a mechanism in which CO₂ molecules are excited by plasma, dissociated into CO in the gas phase and adsorbed on the Ni species of the catalyst as monodentate formates, which were latter transformed into linear carbonyls under plasma assistance. Then, carbonyls were reported to be hydrogenated forming CH species on nickel and, latter, CH₄ [5]. The same authors [6] compared two different configurations of glow discharge plasma systems at low pressure over Ni-based zeolites: In-Plasma Catalysis (IPC, catalyst in direct contact with the glow discharge, which passes through the catalyst bed) and Post-Plasma Catalysis (PPC, plasma generated before the catalyst bed). According to their results, methane production was only possible when CO₂ hydrogenation was performed in IPC mode [6].

However, and even if some authors reported the suitability of Ni-zeolites as catalysts for CO₂ methanation under non-thermal plasma conditions [4–6,27], no indications about the effects of the zeolite structure composition on the catalytic results under atmospheric pressure non-thermal DBD plasma conditions have so far been reported. Thus, the present work studies zeolite-based materials as catalysts for CO₂ methanation under DBD plasma conditions, being the zeolite structure composition and the addition of promoters tested. Indeed, the effects of the zeolite Si/Al ratio and the introduction of Ce will be evaluated. Samples will be also compared with a commercial Ni/ γ -Al₂O₃ catalyst. Catalysts were characterized by ICP, TGA-DSC, XRD, N₂ adsorption, CO₂ adsorption, DRS UV–vis, H₂-TPR and TEM. Thermal tests were also carried out for comparison purposes.

2. Experimental

2.1. Catalysts preparation

The samples prepared and studied in the present work can be found

Table 1
Samples studied in the present work and characteristics in terms of compensating cation, Si/Al_{global} ratio and metals content determined by ICP analysis.

Sample code	Compensating cation	Si/Al _{global}	Si/Al _{framework}	wt.%Ni	wt.%Ce	wt.%Cs
Cs-USY(3)	Cs ⁺	3	4	–	–	14.0
Ni/Cs-USY(3)				15.0		12.0
Cs-USY(38)	Cs ⁺	38	40	–	–	1.5
Ni/Cs-USY(38)				15.0		1.3
Ce-Ni/Cs-USY(38)					20.0	1.0

in Table 1, where data concerning the compensating cation, Si/Al ratio and metal contents are disclosed. The Cs-USY zeolite supports were prepared following procedures already reported in our former studies [28,29]. Indeed, the commercial USY(3) zeolite (Grace Davison, 2.1 wt.% Na⁺ as compensating cation), was firstly ion-exchanged using a NH₄NO₃ solution in order to obtain the H-USY(3) support while the USY(38) zeolite was already provided by Zeolyst in the H-form (wt.% Na < 0.03). Both zeolites were ion-exchanged with a CsNO₃ being the Cs-USY(3) and Cs-USY(38) supports obtained. Then, samples were impregnated with 15 wt.% of Ni by incipient wetness impregnation method, dried overnight at 80 °C and calcined at 500 °C for 6 h under air flow. Additionally, over the Cs-USY(38) support a new preparation was carried out by impregnating 15 wt.% Ni and 20 wt.%Ce, followed by drying and calcination at the same conditions used for Ni/USY samples preparation. Furthermore, one commercial 10%Ni/ γ -Al₂O₃ sample supplied by IBERCAT was tested, in order to compare it with the results obtained for the zeolite-based catalysts.

2.2. Catalysts characterization

Catalysts were characterised by inductively coupled plasma elemental analysis (ICP), thermogravimetric analysis (TGA-DSC), powder X-Ray diffraction (XRD), N₂ sorption, CO₂ adsorption, hydrogen temperature programmed reduction (H₂-TPR), diffuse reflectance spectroscopy UV–vis (DRS UV–vis) and transmission electron microscopy (TEM).

Catalysts elemental analysis was performed by inductively coupled plasma (ICP) in the *Laboratório Central de Análises (Universidade de Aveiro, Portugal)*, in order to determine the composition of the prepared samples in terms of Si, Al, Cs, Ni and Ce (results presented in Table 1).

Thermogravimetric (TGA-DSC) analysis were performed on a Setsys Evolution TGA from Setaram instruments. In the case of the experiments carried out for the determination of the hydrophobicity (h) index [30], samples (0.035–0.040 g) were firstly saturated with water and then heated between 20 and 500 °C (10 °C/min) under air flow (30 ml/min). From the obtained results, h index was determined as the ratio between the registered mass loss at 150 and 400 °C. In the case of the experiments carried out for the identification of carbon deposits in the post-plasma samples, TGA-DSC analysis were carried out again under air flow (30 ml/min) and heating the spent samples (0.035–0.040 mg) from 20 to 800 °C (10 °C/min).

XRD patterns were obtained in a Bruker AXS Advance D8 diffractometer, using Cu K α radiation and operating at 40 kV and 40 mA. The scanning range was set from 5° to 80° (2 θ), with a step size of 0.03°/2 s.

N₂ sorption and CO₂ adsorption measurements were carried out at -196 and 0 °C, respectively, using an Autosorb iQ equipment from Quantachrome. Before adsorption, samples were degassed under vacuum at 90 °C for 1 h and then at 350 °C for 4 h. The total pore volume (V_{total}) was calculated from the adsorbed volume of nitrogen for a relative pressure p/p_0 of 0.95, whereas the micropore volume (V_{micro}) and the external surface area (S_{ext}) were determined using the t-plot method. The mesopore volume (V_{meso}) was given by the difference V_{total} - V_{micro}.

H₂-TPR experiments were performed in a Micromeritics AutoChem II equipment, where the catalysts were, firstly, pre-treated at 250 °C

Download English Version:

<https://daneshyari.com/en/article/6528443>

Download Persian Version:

<https://daneshyari.com/article/6528443>

[Daneshyari.com](https://daneshyari.com)