Ni based CeO_2 catalysts for plasma-assisted CO_2 methanation: On the influence of the catalyst's promotion

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1. Introduction

Nowadays, climate change and global warming are major concerns which are caused by greenhouse gases, and mostly by CO_2. Thus, it is proven that CO_2 emissions produced from fossil fuels are considered the main responsible for climate change [1]. In order to decrease these emissions in the atmosphere, several methods involving Carbon capture and utilization (CCU) or storage (CCS) have been developed in the last decades with different degrees of maturity. CCU techniques can lead to valuable products such as fuels or chemicals. Among all the CO_2 valorization processes, Reverse Water Gas Shift (RWGS) [2] and CO_2 hydrogenation to methanol or methane [3,4] are the most studied from the lab-scale to the final process. Indeed, methanolation and methanation are the solutions which already present higher technology readiness level [5]. Regarding the CO_2 methanation, named also Sabatier's reaction, different types of metal-supported catalysts have been reported. Among them, Ni-based catalysts are the most used ones due to their high activity, their availability, and their lower cost [6]. However, different factors such as the Ni loading, the type of support or the preparation method change their catalytic activity [7]. Within the same approach, different kinds of support have been studied. In particular, cerium oxide (CeO_2), because of its properties such as oxygen mobility, which increases CO_2 activation and hinders carbon deposition, can be considered as a promising support [8]. Moreover, the addition of promoters such as Y, La, Pr or Co was reported as favourable to improve catalysts' activity and stability [6-8,9,10]. Different studies showed an improvement in catalytic performances with the addition of cobalt. Indeed, a report by Alrafei et al. [7] showed that, for Co-Ni/Al_2O_3, nickel dispersion and nickel reducibility improved in the presence of Co. Additionally, in order to improve the catalytic CO_2 methanation process, plasma-assisted catalysis has been studied for more than one decade [11]. Among the types of plasma, the dielectric-barrier discharge (DBD) is the most used in CO_2 methanation studies [13]. Furthermore, Ni-based catalysts are the most commonly used for plasma-assisted catalytic methanation [6]. In terms of promoters, only cerium, lanthanum and cobalt seemed to promote Ni-based catalytic activity for the DBD plasma methanation process over different supports. Recently, it was shown on DBD plasma using ceria-zirconia-based Ni catalysts that the promotion of metals such as La and Y can significantly change both the physicochemical and the electrical features of the catalysts [12]. Herein this study, the catalytic activity of 15 wt% Ni supported on CeO_2 using 1 wt% loading of Co, La, Y and Pr was investigated for CO_2 methanation, and a correlation between structure and activity was proposed.

2. Results and discussion

In this study, Ni-based catalysts were prepared using different promoters, characterized and tested towards plasma catalytic methanation reaction. Catalysts were

prepared via wet impregnation method followed by calcination and, subsequently, reduction and test in a DBD plasma reactor as described elsewhere [8]. Fig. 1 shows CO_2 conversion as a function of the applied voltage (1a), as well as the CO_2 conversion and specific energy input (SEI; corresponding to the input power divided by total flow) as a function of the power (1b) for a constant frequency of 12.3 kHz. It is worth to mention that for all the studied catalysts the CO_2 conversion increased with the applied voltage. As reported in Fig. 1a), the non-promoted catalyst as well as samples promoted with 1 wt% Co, Y, La and Pr show almost the same activity, with a CO_2 conversion of ~80% at higher voltage. However, one can see from the Fig. 1b) that the consumed power for both promoted samples with 1 wt% La and Y is considerably lower than the one observed for the unpromoted catalyst.

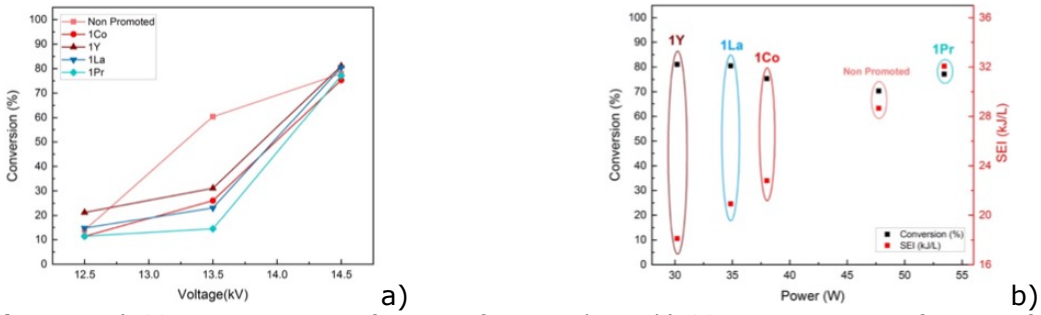

Figure 1. a) CO_2 conversion as a function of input voltage, b) CO_2 conversion as a function of power at 14.5 kV input voltage.

Physicochemical characterizations such as CO_2-TPD showed that the addition of promoters (Y, La and Co) not only increases the total number of basic sites on the catalysts, but also specifically increments the number of medium-strength ones, which are known to be responsible for CO_2 activation in methanation reaction. In this study, among the promoted materials, 1Co15Ni/CeO_2 catalyst showed the highest number of total basic sites as well as the highest number of medium basic ones. Hence, basic sites play an important role in plasma assisted methanation reaction [8]. Furthermore, the synergistic effects could be also an important factor regarding the different behaviour of this catalyst. For example, faster reaction occurrence comes from the lower activation barrier which caused by plasma. Also, in presence of excited species, plasma can change the surface reaction pathway which results in a change in transition state [10].

3. Conclusion

Ni-based catalysts can be considered as proper materials for CO_2 methanation. Adding Co, La and Y as promoters significantly changed the electrical fields of plasma, resulting in a lower energy consumption in DBD plasma-catalytic system. The catalytic performances increased with the addition of these promoters. This increase could be explained by the enhancement of the number of medium basic sites, which are the key factor for CO_2 methanation. 1Co15Ni/CeO_2 catalyst showed the highest number of medium basic sites. Further investigation on electric parameters of these materials is still needed, in order to properly evaluate the synergistic effects in the plasma assisted methanation reaction.

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