

Nickel acetylacetonate grafted on CaO-modified hydroxyapatite catalysts for enhanced performance in decarbonization processes : Effect of Ni loading

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Significance and Relevance

The investigated Ni-Ca-HAP grafted catalysts demonstrate a promising performance in the CO_2 methanation reaction, shedding light on their suitability and competitiveness when compared with reference materials. According to the catalytic activity results, the tested samples achieve their maximum conversion, corresponding to the thermodynamic equilibrium (TE), at relatively low temperatures ($T_{max} \le 425$ °C).

Preferred presentation: (Oral only)

Introduction and Motivations

The use of green hydrogen (GH2) as a fuel is expected to lead the energy transition, proposed as a promising alternative to traditional energy raw materials^{1,2}. However, numerous issues seem to delay the application of GH2 as an energy vector at a large-scale. According to previous reports, components of available natural gas (NG) transmission and distribution networks are incompatible for GH2. Such drawbacks warrant the development of alternative solutions by using NG storage and transport facilities. In this sense, the re-utilization of CO₂, through its catalytic reaction with hydrogen for synthetic NG production, appears to be an attractive strategy.

The efficient catalysts for the CO₂ methanation reaction should be able to reach CO₂ conversions corresponding to TE at low temperatures (< 500 °C) and exhibit a high selectivity towards CH₄ formation^{1,2}. In this sense, Ni-based catalysts have been widely investigated due to their high activity and low-cost. There are, however, a number of drawbacks, which appear to restrict their effective application. For instance, previous studies reported that they might suffer from a rapid deactivation due to a loss in either the number of Ni active sites or the basic sites. Therefore, many studies dealing with the design of novel formulations to provide a suitable interaction metal-support and/or to promote the surface basicity are presently available. For instance, the effect of the addition of some metal oxides (CaO, La₂O₃, CeO₂ and MgO) used as chemical promoters on the activity and stability of the catalysts has been extensively investigated. In addition to their role in providing surface basic properties, they also improve the reducibility, the dispersion of Ni NPs and, thus, their resistance against deactivation.

In this work, a series of nickel acetylacetonate $Ni(acac)_2$ grafted on CaO-modified hydroxyapatite samples are synthesized, characterized and assayed in the CO_2 methanation reaction.

Materials and Methods

The Ca-doped HAP sample presenting 2 wt.% Ca was prepared by impregnation, using a Ca(NO₃)₂·4 H₂O salt solution. The resulting sample was dried at 120 °C, for 12 h and, then, calcined at 500 °C (5 °C min⁻¹) for 4 h. The Ni-Ca-x catalysts were synthesized by grafting method. First, Ni(acac)₂ complex was dissolved in toluene at 60 °C. Thereafter, the solution temperature was adjusted to 30 °C and then 3 g of Ca-modified HAP support was added. The suspension was kept in isothermal conditions, under vigorous stirring, for 3 h. The grafted sample was then (i) filtered, (ii) washed with pure toluene, (iii) dried at 80 °C for 12 h and (iv) finally calcined in air for 4 h at 500 °C (5 °C min⁻¹). The nature of the Ni-support interactions have been investigated by using several characterization techniques, including XRF, DRS, TGA, FRX, FTIR, BET, XRD, CO₂-TPD, H₂-TPR and TEM. The experiments corresponding to the CO₂ methanation reaction were performed in a tubular flow reactor (ID = 9 mm) working at atmospheric pressure. The pre-treatment of the catalysts (500 mg, 160-250 µm) consisted of their reduction at 500 °C under a 20% H₂/N₂ for 1 h and cooling to 200 °C in a flow of N₂. The reaction mixture



was composed of 16% CO₂, 64% H₂ and 20% N₂, with a total flow of 250 cm³ min⁻¹, which corresponds to a WHSV of 30,000 cm³ g⁻¹ h⁻¹. The reaction temperature was sequentially increased, with intervals of 25 °C, from 200 to 500 °C. The analysis system consisted of a gas chromatograph (Agilent 490 Micro GC) equipped with a TCD detector.

Results and Discussion

Table 1 summarizes the chemical, textural and catalytic properties of the grafted catalysts. The efficacy of the grafting process seems to depends on the initial concentration of Ni(acac)₂. The progressive addition of Ni did not affect significantly the textural properties of the HAP support.

Muestra	FRX			BET			Activity
	Nominal wt.% Ni	Actual wt.% Ni	Grafting Yield, %	S_{BET} , m ² g ⁻¹	V_p , cm ³ g ⁻¹	dp, nm	T ₅₀ , °C
HAP	-	-	-	51	0.39	27.7	-
Ni-Ca-0.26	1.9	0.59	30.3	49	0.26	19.7	322
Ni-Ca-0.39	2.9	1.03	36.0	49	0.29	21.7	310
Ni-Ca-0.52	3.8	2.04	54.1	50	0.29	21.6	287
Ni-Ca-0.65	4.7	2.50	53.7	50	0.30	21.0	284
Ni-Ca-0.78	5.5	3.59	64.9	48	0.29	20.0	286

Table 1. Chemical analysis and textural properties of the grafted Ni-Ca-X samples

Fig. 1 shows the light-off curves for all activated Ni-Ca-X samples in the CO₂ methanation reaction. The catalysts were previously activated in a 20% H_2/N_2 flow, at 500 °C for 1 h. The activity of Ni-Ca-0.26 sample starts at 225 °C and increases with the reaction temperature to reach 50% conversion at 325 °C and values close to those of TE at 400 °C. The progressive addition of Ni improves the overall activity, since it systematically decreases the value of T50 (Table 1). Thus, based on the T50 values, the activity follows this general trend: Ni-Ca-0.78 > Ni-Ca-0.65 > Ni-Ca-0.52 > Ni-Ca-0.39 > Ni-Ca-0.26. In parallel, the selectivity of all catalysts approaches 100% in the range of 325-425°C (Fig. 1b). It should be highlighted that the performance of the Ni-Ca-X grafted catalysts clearly outperforms those given over impregnated Ni catalysts used as reference (not shown). This result was associated with the occurrence of suitable properties on the samples prepared by grafting method.



Figure 1. CO₂ conversion and selectivity to CH₄ for Ni-Ca-X grafted catalysts

References

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