Effect of Ni particle size on the efficiency of Ni/HAP catalysts in the decarbonization processes

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Significance and Relevance

The impact of the distribution of Ni NP size on the efficiency of a series of $Ni(acac)_2$/HAP-(x) grafted catalysts in the CO_2 methanation reaction has been studied in the present work. These preliminary study points out that this parameter influences the overall activity. In the range of sizes studied (3.9-6.9 nm), it was found that the efficiency is rather improved over the samples with larger particles.

***Preferred presentation*: (Poster)**

Introduction and Motivations

Amid widespread awareness of the importance of green hydrogen (GH2) in technologies designed to reduce global CO_2 levels to acceptable limits, developing novel approaches for its effective application has become essential. However, one of the most debated challenges consists on identifying solutions for the storage and transportation of GH2. In this context, the methanation of anthropogenic CO_2 emerges as a promising approach, allowing the conversion of GH2 into synthetic natural gas (SNG) and, then, taking advantage of the available SNG infrastructures[1,2].

Therefore, the development of active and selective catalysts is of crucial importance for the CO_2 methanation process. The efficient formulations must be capable to reach conversion values close to thermodynamic equilibrium at low temperatures. In parallel, they should be highly selective to methane production. Ni-based catalysts have been extensively investigated owing to their high activity, selectivity and low cost. Nevertheless, they usually suffer from deactivation due to the occurrence of active phases presenting an inadequate distribution. Previous reports associated the suitability of Ni species with a specific distribution of their particle sizes. Some studies have ascibed the efficiency of Ni to its deposition as small particles, whereas other authors linked the activity to larger particles within a specific range of sizes[3,4].

In this contribution, we present our study on the effect of particle size distribution on the efficiency of Ni species grafted onto hydroxyapatite (HAP) support in the CO_2 methanation reaction. For this, the series of catalysts prepared through grafting method have been calcined at 500 °C, by using different temperature ramping rate (TRR).

Materials and Methods

The Ni/HAP catalysts, presenting around 4.5 wt.% Ni, were synthesized by grafting method. First, $Ni(acac)_2$ precursor was dissolved at 60 °C in toluene. Thereafter, the solution temperature was adjusted to 30 °C before adding 3 g of HAP support. The resulting suspension was filtered, washed with pure toluene and, then, dried at 80 °C for 12 h. Finally, the samples were calcined at 500 °C for 4 h, by using different temperature ramping rate (TRR: from 0.5 to 10 °C min^{-1}). The nature of the Ni-HAP interactions have been investigated by using several characterization techniques, including XRF, DRS, TGA, FRX, FTIR, BET, XRD, CO_2-TPD, TPSR, H_2-TPR and TEM microscopy. The experiments corresponding to the CO_2 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% H_2/N_2 for 1 h and cooling to 200 °C in a flow of N_2. The reaction mixture was composed of 16% CO_2, 64% H_2 and 20% N_2, with a total flow of 250 cm^3 min^{-1}, which corresponds to a WHSV of 30,000 cm^3 g^{-1} h^{-1}. For TOF estimation, additional experiments were performed under

differential reactor conditions in the temperature range of 250-350 °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 properties for the Ni grafted catalysts calcined at 500 ºC with TRR ranging between 0.5-10 °C min^{-1} and reduced at 500 °C (5 °C min^{-1}). The reported data reveal that the particle size generally increases with increasing the temperature ramping rate (3.9 to 6.9 nm). However, no significant change can be observed in the textural properties of the grafted samples.

Table 1. Characterization and activity data for the activated $Ni(acac)_2$/HAP catalysts

Samples	Calcination	TEM	BET			Specific activity	
	Ramping rate, °C min^{-1}	dNi, nm	S_{BET}, $m^2 g^{-1}$	V_p, $cm^3 g^{-1}$	dp, nm	TOF, s^{-1}	Ea, kJ mol^{-1}
HAP		-	51	0.39	27.7	-	-
$Ni(acac)_2$/HAP-(0.5)	0.5	3.9	48	0.34	26.2	0.07	82.3
$Ni(acac)_2$/HAP-(2)	2	5.3	50	0.32	24.4	0.05	84.8
$Ni(acac)_2$/HAP-(5)	5	6.3	50	0.36	25.9	0.11	91.9
$Ni(acac)_2$/HAP-(10)	10	6.9	51	0.33	25.2	0.13	89.1

Fig. 1a displays the evolution of TOF values as a function of the reaction temperature. Unexpectedly, these data point out that the efficiency of Ni species increases with the average particle size increase. Thus, the most efficient catalyst comprises Ni particles exhibiting an average size close to 6.9 nm. Moreover, the activation energy values were estimated from Arrhenius plot (Fig. 1b). According to Table 1, these values are ranging between 82.3 and 91.9 kJ mol^{-1}.

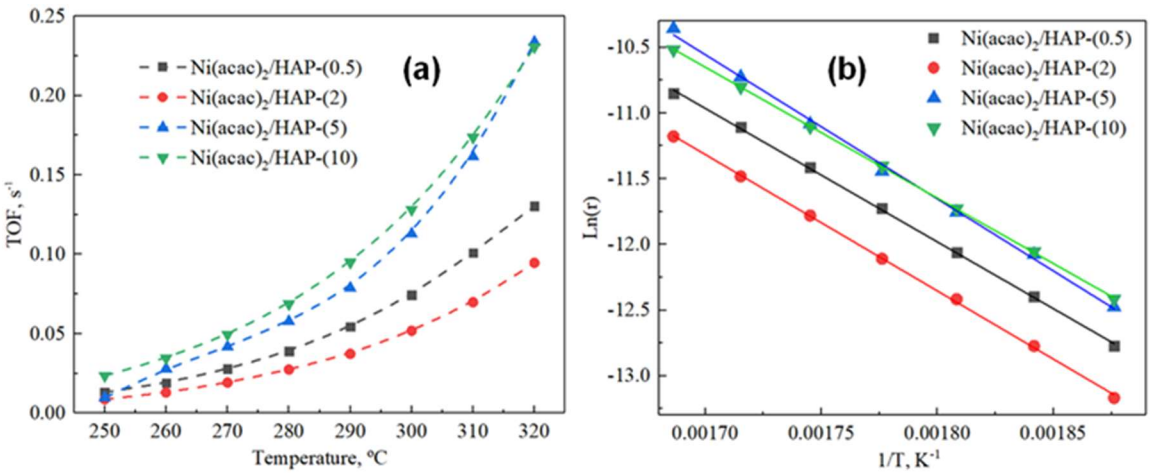

Figure 1. (a) Variation of TOF versus the reaction temperature and (b) Arrhenius plots for the reduced $Ni(acac)_2$/HAP-(x) catalysts

References

1. Z. Boukha, A. Bermejo-López, U. De-La-Torre, J. R. González-Velasco, Appl. Catal. B-Environ. 338 (**2023**) 122989.
2. Z. Boukha, A. Bermejo-López, B. Pereda-Ayo, J. A. González-Marcos, J. R. González-Velasco, Appl. Catal. B-Environ. 314 (**2022**) 121500.
3. N.L. Visser, O. Daoura, P.N. Plessow, L.C.J. Smulders, J.W. de Rijk, J.A. Stewart, B.D. Vandegehuchte, F. Studt, J.E.S. van der Hoeven, P.E. de Jongh, ChemCatChem 14 (**2022**) e202200665.
4. J.K. Kesavan, I. Luisetto, S. Tuti, C. Meneghini, G. Iucci, C. Battocchio, S. Mobilio, S. Casciardi, R. Sisto, J. CO2 Util. 23 (**2018**) 200–211.

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