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# Tri-reforming of methane over a highly-dispersed hydroxyapatite-supported nickel catalyst

Xuan-Huynh Pham<sup>1</sup>, Doan Pham Minh<sup>1\*</sup>

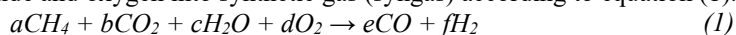
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**Abstract.** Tri-reforming of methane is a promising process to produce synthetic gas *via* the reforming of methane simultaneously with three different oxidants: water vapor, carbon dioxide and oxygen. The thermodynamic aspect of this reaction requires high reaction temperatures (above 700 °C) to reach high methane conversion, while the kinetic aspect requires a solid nickel-based catalyst to reach high reaction rates. Consequently, the solid catalyst used in TRM is exposed to several risks of deactivation, and the development of a performing catalyst is a great challenge for TRM process. In this work, it has been demonstrated that hydroxyapatite (HAP) supported nickel catalyst prepared by ion exchange / ultrasonic vibration led to the formation of nickel nanoparticles and sub-nanoparticles on the HAP support surface, and the resulting catalyst showed very good catalytic performance.

## 1 Introduction

Tri-reforming of methane (TRM) process allows converting a mixture of methane, water vapor, carbon dioxide and oxygen into synthetic gas (syngas) according to equation (1).



Thus, TRM can be applied to various feedstocks such as natural gas, biogas, landfill gas, carbon dioxide captured from the air or from industrial fumes, as well as flue gas [1]. This is particularly interesting since TRM allows valorising all the chemical elements present in these feedstocks. TRM reaction is generally favoured at high temperatures (e.g. > 700 °C) since the reaction is endothermic at low feeding oxygen content [2]. Moreover, TRM needs a solid catalyst in order to reach exploitable kinetics [错误!未定义书签。], [错误!未定义书签。]. Nickel-based catalysts are the most studied catalytic materials in TRM as recently reviewed [错误!未定义书签。], [错误!未定义书签。]. One of the main challenges of TRM catalysts is the deactivation. As reviewed by Pham Minh et al. [错误!未定义书签。], the deactivation of TRM catalysts can be provoked by different reasons: Carbon and coke deposition, thermal sintering, chemical evolution of the catalyst (e.g. dissolution of the active

phase (nickel) in the support, re-oxidation of the active phase, etc.), and catalyst poisoning. Cleaning the feedstocks can prevent the catalyst poisoning. However, for coke deposition, thermal sintering, chemical evolution of the catalyst, it is mandatory to develop efficient TRM catalysts which are active and stable under harsh conditions of TRM process (high temperatures under present of various oxidants).

Recently, hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) appears as a new promising category of catalytic materials [5]. In fact, hydroxyapatite (named thereafter HAP) possesses various physico-chemical properties which are favorable for a catalyst support: good thermal stability, controllable acido-basicity by adjusting the molar ratio of Ca to P, possible high specific surface area with mesoporosity, excellent ion exchange capacity, etc. [错误!未定义书签。]. HAP has been found to be excellent catalyst support in dry reforming of methane [6,7], partial oxidation of methane [8], steam reforming of methane [9]. Recently, HAP supported nickel catalysts have also been demonstrated as efficient catalysts in TRM reaction [10]. In these works, high nickel contents (above 5 wt.%) were usually applied, and thermal sintering of nickel nanoparticles systematically took place, which have also been previously observed for nickel-based catalysts prepared on other catalyst supports [错误!未定义书签。 , 错误!未定义书签。 ,11]. Catalysts containing low nickel contents have never been studied in TRM process, in particular when HAP support is used to disperse nickel active phase. Thus, the present work aims to synthesize a HAP-supported nickel catalyst containing only 1wt.% of nickel under highly-dispersive nanoparticles. This catalyst is the investigated in TRM reaction for syngas production.

## 2 Materials and methods

### 2.1. Catalyst preparation

HAP support used in this work was provided by an industrial partner. This HAP was obtained by coprecipitation using calcium hydroxide and orthophosphoric acid. It has a specific surface area of  $60 \text{ m}^2 \cdot \text{g}^{-1}$  and a molar ratio of Ca/P of 1.67, corresponding to the composition of the stoichiometric HAP.

For nickel deposition on HAP support surface, 5 g of dried HAP were dispersed in 250 mL of de-gassed water. Then, 6.25 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were added to the aqueous suspension of HAP support under stirring (1000 rotations per minute) over night. Then, 200 mL of isopropanol were added to the mixture, followed by 30 minutes of purge under argon flux. After that, the mixture was submitted to an ultrasonic vibration for 3 hours under argon flux. Finally, the solid was recovered by filtration on filter-paper ( $0.45 \mu\text{m}$ ), washed 10 times with water then 3 time with absolute ethanol, and dried overnight at  $105 \text{ }^\circ\text{C}$  in a static oven. The dried catalyst is named Ni/HAP\_D105. Part of this dried catalyst were also reduced under hydrogen atmosphere at  $800 \text{ }^\circ\text{C}$ , and the resulting catalyst is named Ni/HAP\_R800.

### 2.2. Catalyst characterizations

Elemental analysis was carried out by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) with a Jobin Yvon Ultima 2, HORIBA. Temperature programmed reduction (TPR) was performed with a Micromeritics Autochem 2920. Dried catalyst (Ni/HAP\_D105) was heated under a flux of 5% $\text{H}_2/\text{N}_2$  (heating rate  $10 \text{ }^\circ\text{C}$  per minute) from 30 to  $1000 \text{ }^\circ\text{C}$ , and TCD signals were monitored during the heating step. Temperature programmed desorption (TPD) was performed using both carbon dioxide and ammoniac as sensor gases, called respectively  $\text{CO}_2$ -TPD and  $\text{NH}_3$ -TPD. A Micromeritics Autochem 2920 was used for these analyses. For a given TPD experiment, the dried catalyst was first reduced

at 800 °C under hydrogen flux. Then, it was cooled down to 100 °C under He flux. At this temperature, the reduced catalyst was saturated with carbon dioxide or ammoniac. Then, the desorption experiment started by heating the sample (10 °C per minute) up to 800 °C. During the heating, the desorption of carbon dioxide or ammoniac, which was previously adsorbed on the catalyst surface, was monitored *via* TCD signals. Finally, Transmission Electron Microscopy Energy-Dispersive X-Ray Spectroscopy (TEM-EDX) analyses of the fresh and used catalysts were carried out with a JEM-ARM200F Cold FEG microscope.

### 2.3. Catalytic tests

TRM reaction was performed in a fixed-bed reactor having 8 mm internal diameter and 25 cm length. Details of the reactor used have been described elsewhere [错误!未定义书签。]. Briefly, a mixture containing methane, carbon dioxide, oxygen and water vapor were prepared from pure gas bottles and liquid water with the molar ratio of CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O = 1/0.67/0.09/0.85. This mixture was pre-heated at 120 °C before feeding the reactor. For each test, 340 mg of catalyst was used. The catalyst, set at the center of the reactor tube, was pre-treated by in-situ reduction under H<sub>2</sub> flux at 800 °C. At this temperature, the TRM reaction started by feeding the reactor with the gas mixture. The products of the reaction were analysed by a  $\mu$ -GC. Methane and carbon dioxide conversions were calculated as described elsewhere [错误!未定义书签。].

## 3 Results

ICP-AES analysis of the dried catalyst, Ni/HAP\_D105, shows that the nickel loading reached  $1.01 \pm 0.01$  wt.%. Figure 1 (a) presents the TPR profile of the dried catalyst. Several reduction peaks could be observed, suggesting the presence of different nickel species on the surface of HAP support. The strongest peak was centered at 435 °C, which could be due to the reduction of nickel species having strong interaction with the HAP support [12,13]. The other peaks observed within 575 and 885 °C might be attributed to the reduction of nickel species which are incorporated in the apatitic structure of the HAP support [错误!未定义书签。 , 错误!未定义书签。 , 错误!未定义书签。].

Figure 1 (b) shows CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD profiles of the reduced catalyst at 800 °C (Ni/HAP\_R800). NH<sub>3</sub>-TPD curve shows negligible NH<sub>3</sub> desorption, meaning that acid sites were not notably present on HAP support surface. On the other hand, two desorption peaks at around 425 and 450 °C were observed for CO<sub>2</sub>-TPD curve, showing the presence of basic sites. High desorption temperature also indicates the strong basicity strength of these sites.

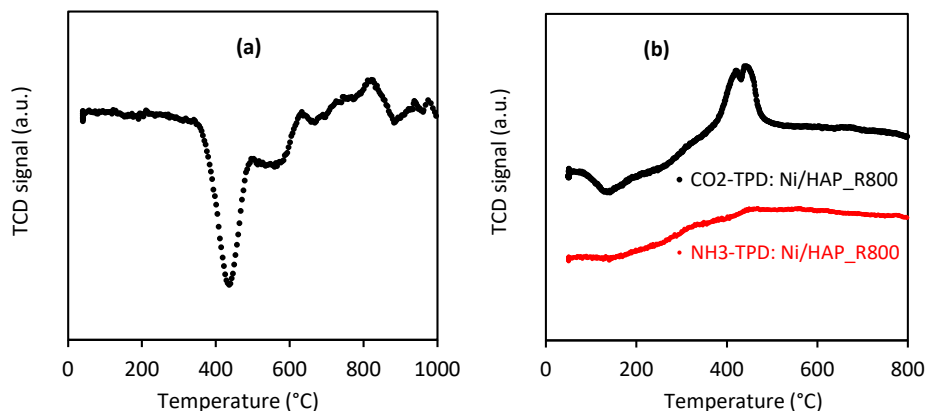


Figure 1. (a) – TPR profile of Ni/HAP\_D105; (b) – TPD of the catalyst reduced at 800 °C (Ni/HAP\_R800).

Figure 2 illustrates TEM images of the fresh Ni/HAP\_R800 catalyst. Nanoparticles of nickel in the range of around 3-20 nm could be easily observed (Figure 2 a, b and c). Particularly, nickel sub-nanoparticles, as well as single nickel atoms seemed to be also formed on the surface of HAP (Figure 2 d). This demonstrates the efficiency of the nickel deposition on HAP surface by ion exchange method followed by a sonication step, for the obtention of highly-dispersed nickel nanoparticles and sub-nanoparticles. The mapping of the main chemical elements in Ni/HAP\_R800 catalyst in Figure 3 help to evidence better the presence of nickel sub-nanoparticles in this catalyst.

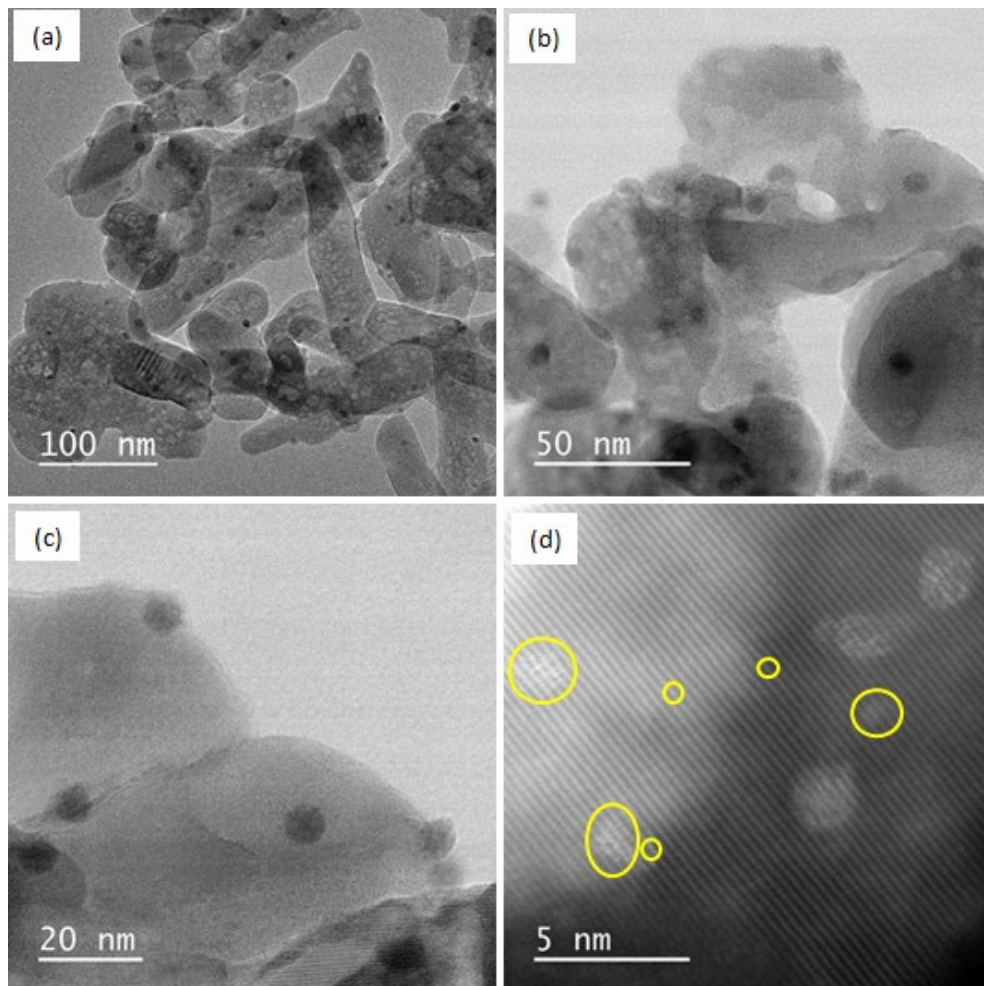


Figure 2. TEM images of the fresh Ni/HAP\_R800 catalyst. Circles: examples of nickel sub-nanoparticles.

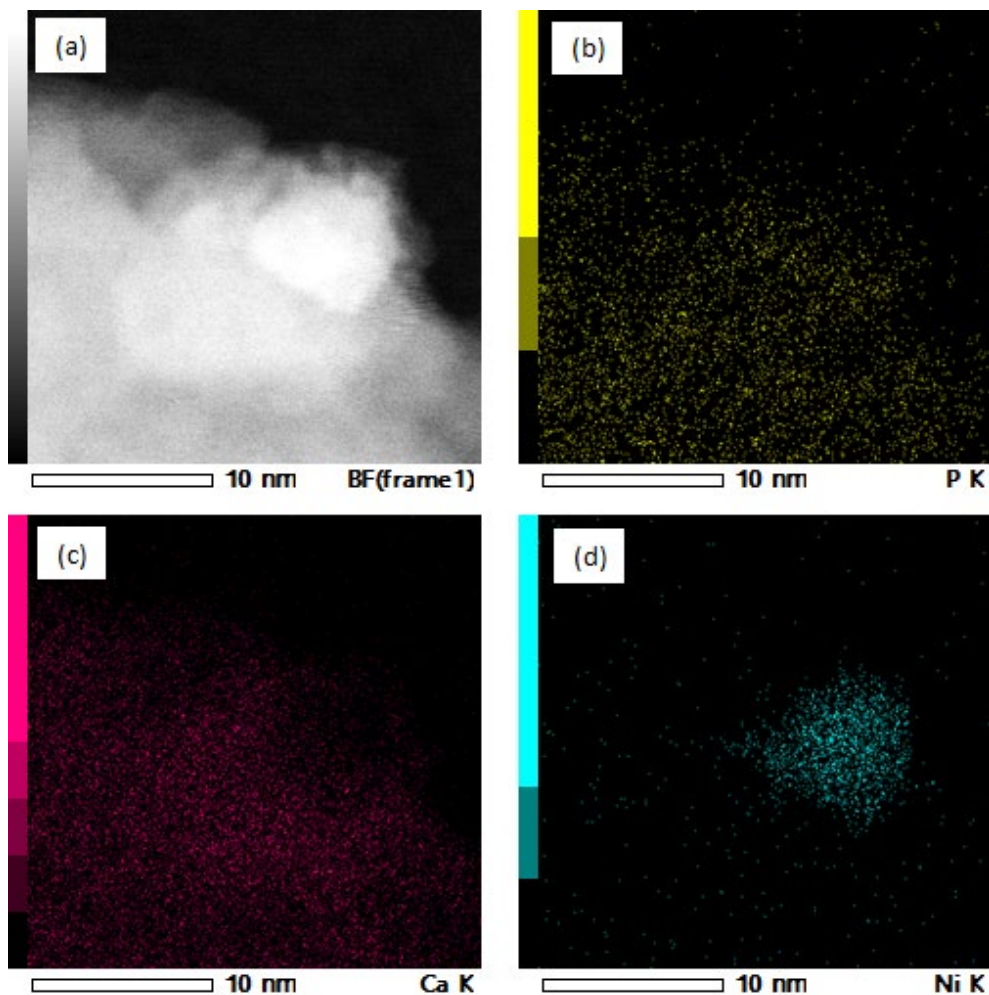
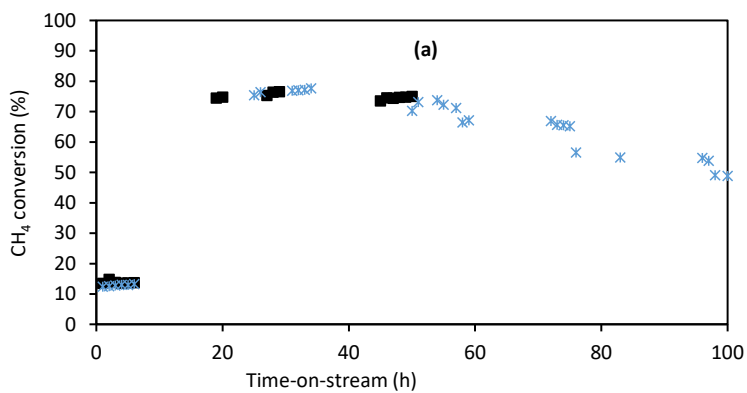


Figure 3. Imaging of phosphorus (b), calcium (c) and nickel (d) on the surface of the fresh Ni/HAP\_R800 catalyst.



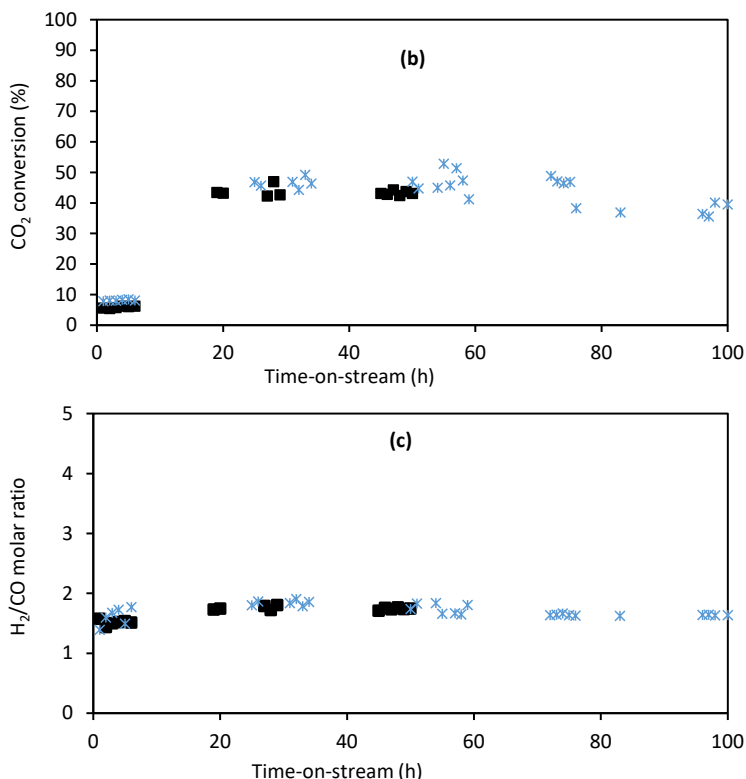


Figure 4. TRM reaction over Ni/HAP\_R800. Reaction conditions: 800 °C, total pressure: 1.5 bar, 340 mg catalyst, molar ratio of the feeding mixture: CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O = 1/0.67/0.09/0.85, feeding flowrate of CH<sub>4</sub>: 45 mL·min<sup>-1</sup> (GHSV: 21006 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>).

Figure 4 shows the results of the catalytic test at 800 °C. The TRM reaction was repeated twice in order to confirm the catalytic behavior. In Figure 4 a, methane conversion started at relatively low value of *ca.* 7%. After around 20 hours-on-stream, methane conversion increased to around 75%, which was kept relatively stable between 20 and 55 hours-on-stream. The increase in methane conversion could probably be due to a re-structuration of the catalyst surface, such as the reduction of Ni(II) species incorporated on the apatitic structure of the HAP support which have not been reduced yet during the in-situ reduction step. It is worth reminding that HAP has excellent ion exchange with bivalent cations such as Ni(II) allowing the incorporation of Ni(II) to the surface of HAP support [错误!未定义书签。]. Within 55-100 hours-on-stream, methane conversion slowly decreased to around 50%, which could be explained by a possible thermal sintering of nickel nanoparticles and sub-nanoparticles. In fact, as highlighted in Figure 5 for TEM analysis of the used catalyst recovered after the catalytic test, large nickel nanoparticles above 20 nm could be observed, indicating this possible thermal sintering. It would be meaningful to better stabilize nickel nanoparticles and sub-nanoparticles on the HAP surface in the future work against thermal sintering. On the other hand, solid carbon seemed to be not formed on the surface of the catalyst after TRM test, which is a very good indicator, since solid carbon deposition is one of the main reasons of the catalyst deactivation in methane reforming process [错误!未定义书签。], 错误!未定义书签。].

Figure 4 b shows the evolution of the carbon dioxide conversion versus reaction time. This profile follows well the evolution of methane conversion in Figure 4 a. This demonstrates that carbon dioxide was well consumed to reform methane into syngas. Finally, Figure 4 c shows the evolution of the molar ratio of  $H_2/CO$ , which was stable around 1.7-1.8.

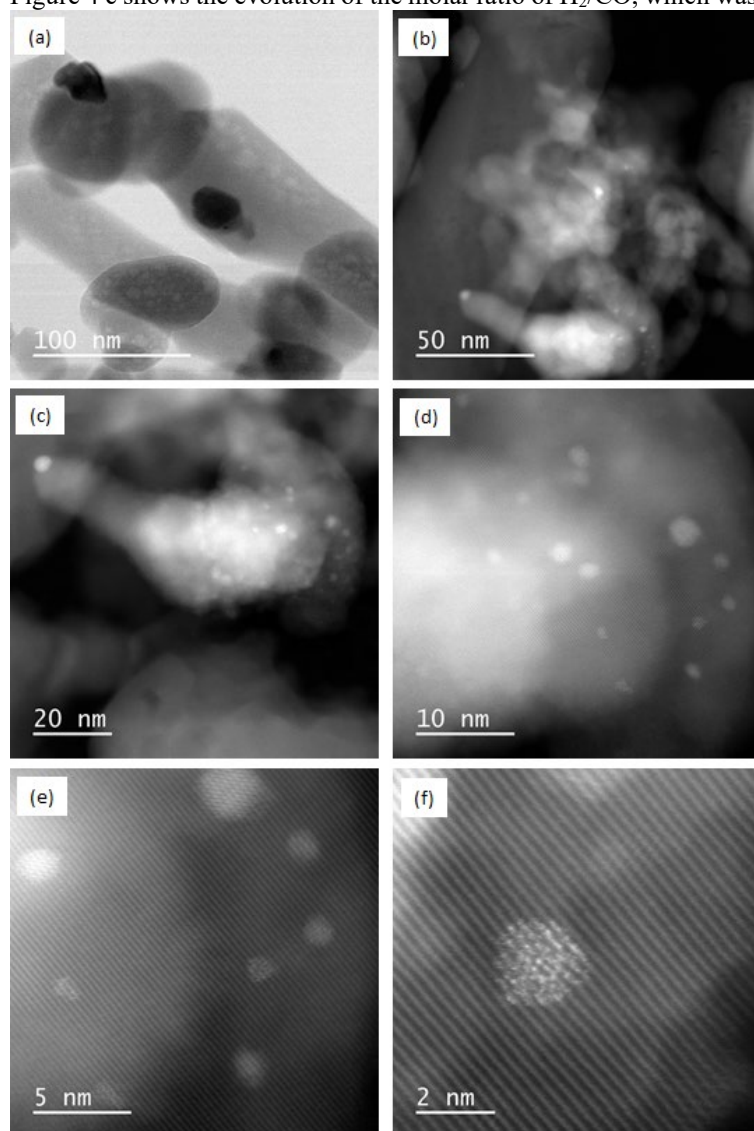


Figure 5. TEM images of the used Ni/HAP\_R800 catalyst, recovered after 100 h-on-stream in TRM at 800 °C and 1.4 bar.

## 4 Conclusions

In this work, we have been successful in the preparation of a highly-dispersed HAP-supported nickel catalyst by ion exchange combined with ultrasonic vibration. Nickel could be deposited on the HAP support under the form of nanoparticles, sub-nanoparticles and even single atoms. In TRM reaction at 800 °C and 1.4 bar, a restructuring of the catalyst surface seemed to take place, enhancing the catalytic activity. Then, a catalytic deactivation took place due to

the thermal sintering of the catalyst at 800 °C. Future work would be focused on the improvement of the stability of nickel nanoparticles and sub-nanoparticles against this thermal sintering, which can allow obtaining very performing TRM catalyst even with low nickel loading of 1wt.%.

## Acknowledgment

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