



Effect of the active metal on the catalytic activity of the titanate nanotubes for dry reforming of methane

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HIGHLIGHTS

- Decoration of Co or Ni into titanate nanotubes and partial incorporation of Pt.
- Transformation of titanate nanotubes during dry reforming of methane.
- Catalytic activity affected by the nature of the active sites.
- Surface Ni^o sites on NiTiO₃ exhibited high CH₄ and CO₂ conversions.

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ABSTRACT

The incorporation of either Co or Ni into titanate nanotubes as well as impregnation of Pt on TNTs were observed in this work. The as-synthesized titanate nanotubes, obtained by hydrothermal method, were *in situ* transformed during dry reforming of methane. All the spent solids were characterized to show the active phase formed during the reaction and the results demonstrated that the catalytic activity was affected by the nature of the active sites. Surface Ni^o sites on NiTiO₃ formed from NiTNT exhibited high CH₄ (30%) and CO₂ (35%) conversions at 600 °C with no deactivation along the reaction time. The nanosized PtO_x particles from PtTNT was lesser susceptible to coking, although sintering remarkably decreased the performance of the solid. On the contrary, severe carbonaceous deposition on Co^o/CoTiO₃ was suggested to be responsible for the deactivation of the solid in dry reforming of methane.

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1. Introduction

The main strategies for upgrading of syngas derived from biogas include its catalytic transformation towards steam reforming, partial oxidation or even dry reforming towards syngas conversion to obtain hydrogen processes [1–6].

Currently, the main process for converting natural gas to synthesis gas is reforming with steam. The steam reforming of methane (SRM) is industrially performed under high temperatures and low pressures viz. 600–900 °C and 1–35 atm, respectively [7–9]. Moreover, the H₂/CO ratio is in the range of about 2.2–4.8 using Pt/Al₂O₃-based catalyst with a relative stability and long lifetime

[2,7]. However, the carbonaceous deposits tend to cover the active sites of catalyst surface during the reaction. Another fact is that the sintering of the particles is also inevitable over Pt/Al₂O₃-based catalysts [2]. Therefore, efforts are being made to turn the process into an environmental friendly reaction working on inexpensive CO₂ methodologies, in designing catalytic dry reforming reactors and demanding cheaper metals for the purpose of optimizing the dry reforming of methane (DRM).

These contributions opened a fascinating catalytic approach, inspiring many researchers to explore new catalytic materials for DRM. In this sense, the demonstrated activity of the supported metals of groups 8 (ruthenium), 9 (cobalt, rhodium and iridium) and 10 (nickel, palladium and platinum) can be further extended towards other methodologies by the exploitation of the aforesaid metals in DRM process [9]. Among these different metals studied so far, Pt, Ni and Co have been of major interest because of their

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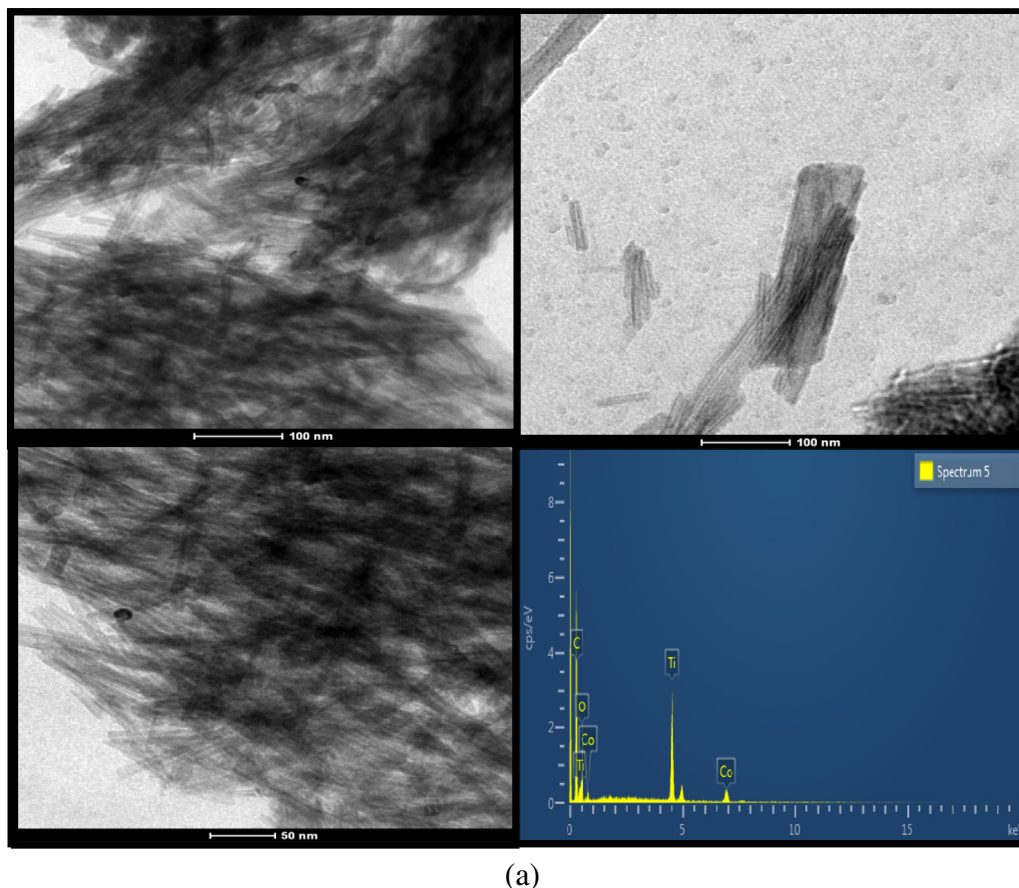


Fig. 1. Transmission electron microscopy images of the solids: (a) CoTNT, (b) NiTNT and (c) PtTNT. The EDS analyses images of the TNTs are also included.

excellent reactivity as active species for the reaction [1–4,7]. The catalytic properties of these active species dispersed on carriers depend on their sizes, shape and reactivity as well.

Nevertheless, the major challenge of using these species in DRM upon using the benchmark alumina support is the deactivation of the solid by methane cracking, Boudouard reaction and CO oxidation [2,10–13], similarly to the SRM. This can hinder the industrialization of DRM process due to possible deactivation of catalysts, their pellets crush as well as increase of the pressure drop and even block of the reactor [12].

Titanate nanotubes (TNT) functionalities give redox and acid-base properties making the interactions between the solid surface and hydrocarbons molecules easy [14–17]. The structural features of TNTs may offer a wide array of conversion and selectivity by tailoring the morphology and functionalities on the surface.

The use of TNTs as catalysts carriers has been investigated for water gas shift reaction, reduction, steam reforming of hydrocarbons, hydrogenation reactions and CO oxidation, among others [14–19]. By virtue of the intercalation of metal cations in TNTs and/or decoration of metal oxides nanoparticles procedures, the as-synthesized TNTs give *in situ* transformation to form active centers on supported catalysts.

Thus, the remarkable catalytic performance of TNT-based catalysts in DRM reaction is studied in this work. The features of the TNTs include, but are not limited to larger specific surface area, pore volume and redox abilities. Although the traditional noble metal-based catalysts are generally reported more active toward CH_4 and CO_2 conversion and less sensitive to carbon deposition,

their application is confined by high cost and limited availability, in opposite do the TNTs nanomaterials.

2. Experimental

2.1. Catalyst preparation

The solids were prepared according to the method previously described [14]. Briefly, anatase TiO_2 powder (1.14 g, Aldrich) was mixed with 35 mL de NaOH 10 mol L^{-1} in a 100 mL Teflon container and the mixture was kept at 160°C for 72 h in an autoclave. Subsequently, the resulting mixture was filtered to dryness by vacuum filtration to yield a paste, which was thoroughly washed for several times with deionized water. Then, the solid was dried at 50°C for 72 h to produce the sodium-containing trititanate nanotubes.

Modified nanotubes, designated as CoTNT and NiTNT were prepared by ion exchange. The required amount to have either cobalt or nickel was added using aqueous solutions of the nitrate salts of the corresponding metal cation to achieve the additive metal loading of 1.8 wt% in each case.

The incipient wetness impregnation method was adopted to incorporate platinum on TNT. This solid was first mixed with 60 mL of deionized water in a flask to generate a suspension. The calculated volume of 1.0 mmol L^{-1} H_2PtCl_6 (Aldrich) was slowly added to the suspension and stirred for 2 h at room temperature in a rotary evaporator with a water bath at 80°C . The resulting

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