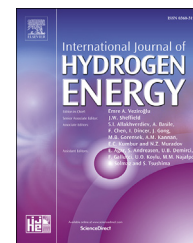


Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Ceria and zirconia modified natural clay based nickel catalysts for dry reforming of methane

Hongrui Liu ^{a,b}, Patrick Da Costa ^{a,b,*}, Haithem Bel Hadj Taief ^c,
Mourad Benzina ^c, Maria Elena Gálvez ^{a,b}

^a Sorbonne Universités, UPMC, Univ. Paris 6, Institut Jean Le Rond d'Alembert, 2 place de la gare de ceinture, 78210 Saint-Cyr-L'Ecole, France

^b CNRS, UMR 7190, Institut Jean Le Rond d'Alembert, 2 place de la gare de ceinture, 78210 Saint-Cyr-L'Ecole, France

^c Laboratoire Eau, Energie et Environnement (LR3E), Code: AD-10-02, Ecole Nationale d'Ingénieurs de Sfax, Université de Sfax, B.P.1173.W.3038 Sfax, Tunisia

ARTICLE INFO

Article history:

Received 7 November 2016

Received in revised form

27 December 2016

Accepted 11 January 2017

Available online 4 February 2017

Keywords:

Natural clay

Ni catalysts

Hydrogen

Syngas

Dry reforming

Promoters

ABSTRACT

Ce and Zr promoted Fe/Cu-modified natural clay based catalysts were prepared and tested in dry reforming of methane (DRM) at temperatures from 600 to 800 °C. The physico-chemical properties of these catalysts were analyzed by means of N₂ adsorption, X-ray diffraction (XRD). H₂-temperature programmed reduction (H₂-TPR) and CO₂-temperature programmed desorption (TPD). Ce and Zr promotion resulted in a considerable increase of the catalytic activity. This increase can be mainly ascribed to an improved reducibility of Ni species, together with slightly higher Ni⁰ crystal size, that, on the other hand, also catalyze undesired parallel reactions resulting in carbon formation, such as direct methane decomposition. Both Ce and Zr presence also promoted the presence of weak and medium strength basic sites, which are thought to favor CO₂ adsorption and desorption on the catalyst surface, leading to enhanced catalytic activity.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Natural gas, mainly composed of methane, is thought to play an important role in our transition to a future renewable-based scenario. By means of the well-known steam methane reforming process (SMR), it is moreover the source for the production of industrial hydrogen, as well as of synthesis gas: mixture of H₂ and CO employed in methanol or liquid fuel synthesis. Still, methane is quite a rough molecule to activate,

since it contains four highly stable C–H bonds [1,2]. Dry methane reforming (DMR) has been lately proposed as an alternative to steam reforming, encompassing CO₂ valorization. DRM is only thermodynamically possible at temperatures higher than 650 °C and it is additionally strongly kinetically hindered. High temperatures and the use of an active and selective catalyst are therefore required in order to get acceptable syngas yields. Moreover, several concomitant reactions, such as reverse water gas shift (RWGS) and direct carbon decomposition, may occur to a greater extent than the

* Corresponding author. Sorbonne Universités, UPMC, Univ. Paris 6, Institut Jean Le Rond d'Alembert, 2 place de la gare de ceinture, 78210 Saint-Cyr-L'Ecole, France. Fax: +33 1 30854899.

E-mail address: patrick.da_costa@upmc.fr (P. Da Costa).

<http://dx.doi.org/10.1016/j.ijhydene.2017.01.075>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

DRM reaction itself. Among them, direct methane decomposition, resulting in carbon formation and deposition, i.e. coking, posing a real challenge in terms of catalytic stability. Still, dry reforming of methane yields an equimolar mixture of H₂ and CO, suitable for direct Fischer–Tropsch synthesis [3–5], and simultaneously consumes methane and CO₂, which are furthermore two important greenhouse gases.

Although noble metal based catalysts, such as Pt, Rh and Ru, evidence very high activity and selectivity, together with good resistance to coking [6–8], they are scarce and considerably expensive. Nickel-based catalysts are generally preferred and have become the most widely used catalysts in DRM, since they exhibit similar activity and have much lower cost. However, the deactivation of Ni-based catalysts due to carbon deposition remains an issue, together with Ni sintering taking place at relatively low temperatures, especially in the presence of CO [9,10].

The support plays an important role in the preparation of efficient DRM catalysts. It influences the dispersion of the active phase, not only providing adequate textural properties, i.e. high specific surface area, but also enhancing the interaction with the metallic phase, and/or the adsorption of the reactants, through the presence of surface basic groups. Among the different possible materials, natural clays have recently attracted considerable attention due to their high availability and to their unique and adjustable physico-chemical properties [11,12]. Natural clays have been more-over considered as supports in the preparation of DRM catalysts. Gamba et al. [11] used an Al-modified mineral clay in the preparation of Ni-based catalysts promoted with Pr that turned out to be considerably active in DRM while leading to a low extent of carbon deposition. Wang et al. [13] employed different natural clays (montmorillonite and bentonite) in view of their particular pore structure and surface properties. They remarked that this kind of materials could be promising supports for the preparation of DRM catalysts. However, and contrarily to the observations made by Gamba and co-workers, they also claimed that carbon formation and deposition in the presence of such natural clay-based catalysts needed to be further controlled.

The addition of different promoters has been considered as a way of improving the DRM catalytic performance. Particularly, Ce and Zr oxides have been widely used for the promotion of DRM catalysts. Their presence has been generally linked to increased stability, either by means of the inhibition of carbon-forming side reactions, or due to their participation in the gasification of the already formed carbon deposits. Regarding the promotion of natural clay-based catalysts, Osawa et al. [14] studied the effect of Ce incorporation into several illite clay-supported catalysts for DRM. They showed that the presence of Ce enhanced Ni dispersion on the clay surface. Daza et al. [15] reported an important beneficial effect of the presence of Ce on the activity and selectivity of mineral clay-supported Ni-catalysts, as well as a diminution in the formation of coke, that however depended on the nominal amount of Ce used. To the best of our knowledge, no studies have been published in the exiting literature reporting the promotion of natural clay-based catalysts with Zr oxides. The use of Zr as a promoter is however promising. Liu et al. [16] showed that Zr promoted the catalytic activity of a

mesoporous silica-supported catalyst through the enhancement of their structural stability and the improvement of Ni dispersion, which contributed to the partial activation of CO₂. The promoting effect depended however on the clay composition and thus its origin.

In the present work, Fe and Cu modified natural clays were used in the preparation of Ni catalysts that were further promoted using Ce and Zr oxides. The presence of Fe and Cu pillars may influence not only the type of porosity of the support, and therefore Ni distribution and catalyst stability, but also the activity and selectivity of these materials, due to the inherent presence of Fe and Cu together with Ni. Ceria and zirconia may help controlling coke formation and deposition, improving the catalytic stability.

Experimental

Preparation of the Fe and Cu modified clay supports

A natural clay from the deposit of Jebel Cherahil (Kairouan, Central-West of Tunisia) was chosen as the raw material. The procedure for the purification and Na-ion exchange of the raw clay are carefully described in Refs. [17,18]. For the preparation of the Fe-modified clay, a pillaring solution was prepared by slow addition of Na₂CO₃ powder (97%, MERCK) into a 0.2 M solution of Fe(NO₃)₃ (Fe(NO₃)₃·9H₂O 97%, MERCK) while stirring at 100 rpm for 2 h at room temperature, until a molar ratio Fe/Na₂CO₃ of 1:5 was reached. The solution was then aged during 4 days at 60 °C. The resulting oligomeric Fe (III) solution was added stepwise into a 2% wt. aqueous dispersion of the purified Na-exchanged clay. The dispersion was stirred at 100 rpm for 24 h, then filtered, washed by with deionized water, and finally centrifuged at 4000 rpm for 10 min. The resulting solid material was calcined at 300 °C for 24 h, and ground to 100-mesh. For the preparation of the Cu-modified clay, 1 g purified clay was added to 100 mL of 0.02 M copper acetate solution (Cu(CH₃COO)₂ (98%) MERCK). The suspension was stirred at a pH of 5.2 and 40 °C for 24 h. The modified clay was then separated by centrifugation, washed with distilled water, dried at 60 °C for 24 h and finally calcined at 400 °C for 5 h. Note here that the iron content upon pillaring increased from 7.7% to 32.5% (wt.% Fe₂O₃, as determined by means of XRF), whereas Cu content increased from almost zero to 11.1% (wt.% CuO). The XRD pattern of the raw clay evidenced the presence of smectite (montmorillonite) associated with illite and kaolinite [17].

Catalysts preparation

Nickel was introduced into each clay support by means of a conventional impregnation method, using an aqueous solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Aldrich) as metal precursor. The Ni loading for all catalysts was fixed as 15% wt. Upon impregnation, the catalysts were dried overnight at 100 °C and subsequently calcined at 550 °C for 4 h. 10% wt. Ce and Zr were added to the catalyst formulation also by means of a conventional impregnation procedure, respectively using CeN₃O₉·6H₂O and ZrO(NO₃)₂·6H₂O as precursors. Upon 2 h stirring, the suspension dried at 40 °C in rotary

Download English Version:

<https://daneshyari.com/en/article/5145520>

Download Persian Version:

<https://daneshyari.com/article/5145520>

[Daneshyari.com](https://daneshyari.com)