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Natural clay-based Ni-catalysts for dry reforming of methane at moderate temperatures

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ABSTRACT

Natural clay based Ni-containing catalysts for dry methane reforming (DRM) were prepared using a Fe and Cu-modified Tunisian clay as support. The catalysts were characterized by means of X-ray diffraction (XRD). H_2-temperature programmed reduction (H_2-TPR) and CO_2-temperature programmed desorption (TPD). The catalysts were either reduced at 800 or at 900 °C prior to the DRM tests. Reduction temperature has a determinant influence in Ni crystal size and basicity. The catalysts reduced at 800 °C showed better catalytic performance than those reduced at 900 °C. The catalysts prepared using the Cu-modified clay yielded the highest CO_2 and methane conversions all the time. At 850 °C, 72% CO_2 conversion was measured, corresponding to a H_2/CO ratio near 1, close to the thermodynamically forecasted value.

1. Introduction

Dry reforming of methane (DRM) has received considerable attention in the last years, as one of the most promising routes for CO_2 valorization [1,2]. It involves consumption of two important greenhouse gases methane and CO_2, resulting in the formation of a syngas ($CO + H_2$ gas mixture) having a H_2/CO ratio equal to 1, ideal for liquid fuel synthesis through Fischer-Tropsch or for chemical synthesis through hydroformylation [3]. DRM is nevertheless an endothermic reaction ($\Delta H^0{}_{298K} = +247\ \mathrm{kJ\,mol^{-1}}$) that is only thermodynamically favorable at moderate-high temperatures (>750 °C). At these moderate-high temperatures the reaction is still kinetically slow and only takes place in the presence of a catalyst, i.e. Ni-containing catalyst, preferred to noble metal-based ones due to lower cost and higher availability. In the whole range of reaction temperatures but especially at low-moderate reaction temperatures (<750 °C) carbon forming reactions are bound to take place, among other side reactions, resulting in the formation of deposition of carbon on the catalyst surface. This problem of catalyst deactivation needs to be assessed in order to increase the stability of the catalytic system in view of its practical utilization. Different approaches, in terms of the utilization of nano-structured supports [4,5], and in terms of increasing the dispersion and controlling the crystal size of the Ni particles deposited on the catalysts surface [6,7], proof the possibility of tailoring the selectivity of the DRM reaction with the final aim of minimizing carbon deposition.

In general, the support itself is not catalytically active, however it may strongly influence the catalytic performance of the overall catalytic system. Dependent on the type of support used, the interaction active phase-support may be favored, it can also provide acid or basic sites that may promote the adsorption of reaction species, and furthermore, it offers adequate surface area and may improve the mechanical properties of the catalytic system. Clays have been widely used as supports for the preparation of diverse catalysts, including Ni-containing catalyst for dry methane reforming. Among them, synthetic clays, i.e. hydrotalcites, have shown to yield high activity, selectivity and catalytic stability in DRM, since they provide adequate surface area, mostly in terms of mesopores and intrinsic surface basicity, resulting in enhanced Ni dispersion and reducibility [6–9]. Natural clays stand as a most interesting option, since they are naturally available, green and low-cost materials. They have been recently used as supports in several catalytic applications [10–15], including DRM [15–20]. Either raw [15] or Al-pillared [16] smectites were used for in the preparation of Ni-based catalysts for DRM. Daza et al. [17], Wang et al. [18], and Barama et al. [19] considered the utilization of raw, LaAl and Al-pillared

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montmorillonites. Hao et al. [20] employed a Zr-pillared laponites. All these works point out the benefits of using these natural clays as supports in the preparation of DRM catalysts. Moreover Wang et al. reported a direct influence of the mesoporous surface area of LaAl-pillared clays on their activity, in terms of methane conversion [18].

The use of natural Fe or Cu-pillared clays as supports in the preparation of Ni-based catalysts for DRM has never been described in the existing literature. 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. The present paper describes the DRM behavior of Ni-catalysts prepared using a raw, Fe-pillared and Cu-pillared natural clay. The so-prepared catalysts were characterized from a physico-chemical point of view with the aim of assessing the influence of important properties such as porosity, Ni distribution and crystal size, as well as basicity, for two different reduction temperatures, i.e. 800 and 900 °C.

2. Experimental

2.1. Preparation of the clay-based catalysts

A natural clay from the deposit of Jebal Cherahil (Kairouan, Central-West of Tunisia) was chosen as the raw material. The procedure for its purification and Na-ion exchange of its surface have been previously described elsewhere [14,21]. The Fe-pillared clay, Fe-Clay, was synthesized as described in detail in our previously published work [21]. The pillaring solution was prepared by slow addition of Na_2CO_3 powder (97%, MERCK) into a 0.2 M solution of $Fe(NO_3)_3$ ($Fe(NO_3)_3{\cdot}9H_2O$ 97%, MERCK) while stirring at 100 rpm for 2 h at room temperature until the molar ratio Fe/Na_2CO_3 reached 1:5. The solution was then aged during 4 days at 60 °C. Finally, the resulting oligomeric Fe(III) solution was added into a 2% wt. aqueous dispersion of the purified Na-exchanged clay, at a ratio of 10^{-3} mol of Fe^{3+} per gram of clay. The dispersion was agitated at 100 rpm for 24 h, then filtered, washed by with deionized water several times, and finally centrifuged at 4000 rpm for 10 min. The resulting solid material was calcined at 300 °C for 24 h, and subsequently ground to 100-mesh. For the preparation of the Cu-pillared clay, Cu-Clay, 1 g of Na-exchanged raw clay and 100 mL of 0.02 M copper acetate ($Cu(CH_3COO)_2$ (98%) MERCK) solution were stirred at a pH of 5.2 and 40 °C for 24 h. The resulting suspension was filtered and the precipitate was washed several times with deionized water. The catalyst was then dried at 120 °C for 12 h and subsequently calcined at 400 °C for 5 h. The composition of raw, Fe and Cu-pillared clays are shown in Table 1.

Nickel was introduced into each clay support by means of a conventional impregnation method, using an aqueous solution of nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, 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.

2.2. Physicochemical characterization

The chemical composition of the natural and modified clays was analyzed by means of X-ray fluorescence (XRF, ARL1 9800 XP spectrometer). The textural properties of both the clay supports and the catalysts were studied by means of N_2 adsorption at −196 °C (ASAP 2020, Micromeritics). The samples were previously degased at 250 °C. X-ray diffraction (XRD) patterns were obtained in a PANalytical-Empyrean diffractometer, equipped with CuK_α ($\lambda = 1.5406$ Å) radiation source and 2θ range between 3 and 90°, with a step size of 0.02°/s. The Scherrer equation was used for calculating the crystal size of nickel on the reduced clay based catalyts. The profiles of temperature-programmed reduction (H_2-TPR) were acquired in a BELCAT-M (BEL Japan) device, equipped with a thermal conductivity detector (TCD). The calcined clay-based catalysts were first outgassed at 100 °C for 2 h, then reduced in 5% (vol.) H_2/Ar, while the temperature was increased from 100 °C to 900 °C at a heating rate of 7.5 °C/min. The same apparatus was used for the acquisition of the CO_2-TPD profiles. The materials were first degassed for 2 h at 500 °C at a heating rate of 10 °C/min, cooled to 80 °C in pure helium, and subsequently exposed to a gaseous mixture of CO_2 (10 vol.%)/He for 1 h. Helium was then flown for 15 min in order to desorb the physically adsorbed CO_2. Temperature programmed desorption (TPD) of CO_2 was carried out heating the samples at 10 °C/min up to 950 °C under He flow. The desorbed CO_2 was measured with the aid of the TCD detector.

2.3. Catalytic DRM experiments

The DRM experiments were carried out in a tubular quartz reactor (8 mm internal diameter) at temperatures from 850 °C to 600 °C, under 100 mL/min reactant gas flow (GHSV = 20,000 h^-1), composed of $CH_4/CO_2/Ar = 1/1/8$. The catalyst was submitted to each reaction temperature during at least 30 min reaction time, and until steady state conversions were reached. An overall time-on-stream of 5 h can be considered for all the catalysts tested. Prior to DRM experiment the calcined catalysts were reduced in situ either at 800 °C and 900 °C, for 1 h in a stream of 5% (vol.) H_2/Ar. These reduction temperatures were chosen at the sight of the H_2-TPR profiles obtained for the catalysts. Though, in principle, 800 °C reduction temperature would be enough, the catalysts were as well reduced at 900 °C, due to the slight tailing of the last peak observed in the TPR profile acquired for the Ni/Clay catalyst. The compositions of the products were analyzed in a gas chromatograph (Varian GC4900), equipped with a thermal conductivity detector. The conversions of CO_2 and CH_4, as well as the ratio H_2/CO were calculated as follows:

$$X_{CO_2} = (n^{in}_{CO_2} - n^{out}_{CO_2})/n^{in}_{CO_2} \times 100 \qquad (1)$$

$$X_{CH_4} = (n^{in}_{CH_4} - n^{out}_{CH_4})/n^{in}_{CH_4} \times 100 \qquad (2)$$

$$H_2/CO = n^{out}_{H_2}/n^{out}_{CO} \qquad (3)$$

Where n^{in}_i and n^{out}_i denote the concentration for each species entering and exiting the reactor.

3. Results and discussion

3.1. Textural, structural and chemical properties of the natural clay based Ni-catalysts

Table 2 contains the results of the textural characterization of the clays and natural clay based Ni-catalysts, performed by means of N_2 adsorption. The adsorption isotherms obtained (Fig. 1) correspond to type IV isotherms, according to IUPAC classification, presenting H3 hysteresis loops, typical of laminar-structured materials containing slit-shaped pores. They all show a strong increase of adsorption at high relative pressured, linked to the presence of macropores. The desorption branch of the isotherms closes at low relative pressures (below 0.4), pointing to impeded diffusion and trapping of N_2 molecules inside the partially collapsed and far too complex laminar structure, maybe as a consequence of an excess of Fe and Cu pillars. The excess of Fe pillars is clear at the sight of the lower surface area of this material, vis-à-vis the non-modified clay: some pores remain blocked, maybe also due to the effect of a partial collapse of the pillars.

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