

Ni/ γ -Al₂O₃ catalyst from kaolinite for the dry reforming of methane

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Abstract

A catalyst consisting of a 5% Ni over a γ -Al₂O₃ novel support was evaluated under high-temperature reaction conditions. The γ -Al₂O₃-rich phase was obtained by selective dissolution of siliceous components of heat-treated kaolinite. The support was appropriate to prepare a catalyst with high surface area (170 m²/g) that showed to be active and stable for dry reforming of methane at 650 °C and a CH₄/CO₂=0.5 molar ratio. Compared to the conventional Ni/ α -Al₂O₃ catalyst, this new material showed an improved sulfur resistance when it was reduced in hydrogen steam at the reaction temperature. In industrial conditions, CH₄/CO₂=1, deactivation by carbon deposition was not increased. The content and type of deposited carbon were analyzed by TPH and TPO techniques. As regeneration methods of the coked catalysts, hydrogen and oxygen carbon treatments were employed. After the treatment with hydrogen the catalyst reaches the initial activity, but with oxygen the activity only is partially regenerated.

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1. Introduction

Nickel supported on alumina catalysts is employed in the industry for the CO₂ reforming of methane in the obtention of syngas [1]. The higher temperatures necessary for this endothermic process are a problem for working with thermostable catalysts containing high surface area. Previous works have shown that the addition of aluminium to α -Al₂O₃ [2,3] increase the surface area and improve the stability and activity the in Ni-alumina catalysts for the methane oxidation and reforming reactions.

The γ -Al₂O₃ phase obtained by selective dissolution of siliceous components of kaolin clays thermally amorphized has high surface area and great thermal stability. These are the desired characteristics when catalytic supports are used in high-temperature reactions. Between these reactions, the dry reforming of methane is an attractive reaction for various industrial (obtention of oxoalcohols, fertilizing, Fisher–Tropsch synthesis, etc.) and environmental applications (CH₄ and CO₂ elimination) over metal-supported catalysts. Metals as Ni, Co, Fe, etc., have shown to be very

useful for the dry reforming of methane, especially for their high activity and low price. The most important requirement for the competitive commercial reforming catalysts is their stability and resistance to deactivation by sulfur and carbon.

On the basis of those ideas, we studied a new Ni-supported catalyst. The novel support, principally γ -Al₂O₃, obtained from kaolinite, is appropriated for the preparation of active, selective and stable catalysts for the dry reforming of methane. This catalyst is compared with Ni/ α -Al₂O₃ catalysts previously studied.

2. Experimental

2.1. Obtention of γ -Al₂O₃ by alkaline lixiviation

A kaolinite, 6 T (Georgia, USA) thermally treated was used to prepare a γ -Al₂O₃ phase. Sample was lixiviated in 4 M OHK (Carlo Erba, p.a.) solutions. First, the solid was crushed to 30–40 mesh (420–595 μ m) and was calcined at 980 °C for 24 h. Lixivate was obtained by mixing 1 g of kaolin clay with 250 ml of OHK solution; suspension was digested at 90 °C for 1 h under agitation. After lixiviation, both phases were separated by filtration. Solid was washed with 0.5 M OHK solution then washed several times with

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Table 1
Chemical composition of kaolinite and support

Sample	Al ₂ O ₃ (%)	SiO ₂ (%)	TiO ₂ (%)	Fe ₂ O ₃ (%)	K ₂ O (%)
Kaolinite	41	55	1.77	1.34	0.13
Support	76	18	2.8	1.7	–

distilled water, dried at 110 °C and finally calcined at 800 °C, 1 h. The solid obtained presents a surface area of 170 m²/g and a pore volume of 0.653 cm³/g. The chemical composition of original kaolinite and the support were shown in Table 1.

2.2. Preparation of catalyst

Catalysts containing 5% of Ni were prepared by impregnation of new support (γ -Al₂O₃) with aqueous solution of nickel nitrate (Ni(NO₃)₂·6H₂O). After impregnation, the samples were dried at 100 °C during 1 h and calcined in air at 600 °C for 2 h. Finally, precursors were activated by reduction in 100 cm³/min H₂ stream at 650 °C and a heating rate of 10 °C/min, 1 h. The catalytic properties of this new catalyst, named (Ni/ γ -Al₂O₃)_k, was compared with the Al-promoted (Ni-Al/ α -Al₂O₃) and -unpromoted (Ni/ α -Al₂O₃) catalysts.

2.3. Catalysts characterization

The catalysts, fresh and extracted of reactor, were characterised by gas adsorption, temperature-programmed analysis (TPR, TGO, TPH) and X-ray diffraction (XRD).

The identification of crystalline phases and the Ni crystal size were determined, on reduced samples, by XRD using a Philips PW 1740 equipment, with Cu K α radiation (λ =1.5418 Å). The mean size of the nickel particles was determined by XRD line broadening (dp_{sch}) using the Scherrer equation [12].

The BET surface area and pore volume distribution were measured by nitrogen adsorption at –196 °C using an Accusorb 2100E Micromeritics analyzer. Samples were outgassed at 100 °C during 12 h before adsorption.

The CO₂ reforming of methane tests were carried out in a flow reactor with on-line chromatograph at 650 °C, atmospheric pressure and a total flow rate between 160 and 200 cm³/min. A fixed bed quartz reactor containing 0.02 g of catalyst was employed. The absence of diffusional effects was verified as described in Ref. [6].

Stability test was determined at 650 °C during 20 h. The feed and effluent of the reactor were analysed in a Perkin-Elmer Sigma I gas chromatograph. A 3-m Porapack Q column and a TCD were used at 40 °C in a He flow of 40 cm³/min.

After the catalytic test, the reactor was cooled in reaction mixture from 650 to 70 °C, so as to avoid carbon gasification. The reactor was then cooled down to room temperature and purged in hydrogen flow for 12 h. In a subsequent stage,

in situ TPH was carried out over the tested samples. The reactor was heated at a linear rate of 10 °C/min from room temperature to 800 °C in an hydrogen flow rate of 20 cm³/min while monitoring the effluent gas composition by flame ionization detector (FID).

The reactivity of the carbon species was analyzed by temperature-programmed oxidation (TPO). The experiments were carried out in a Shimadzu TGA-50H under air stream (20 cm³/min) by increasing the temperature from RT to 800 °C at a heating rate of 10 °C/min.

Thioresistance was determined by adding 0.2 ppm of H₂S to the reactor feed and operated in the same conditions of temperature and flow rate.

3. Results and discussion

3.1. Catalytic activity and stability

Table 2 shows the effect of the supports on the conversion of methane and CO₂ for the catalysts of Ni supported on commercial α -Al₂O₃ (Ni/ α -Al₂O₃), the Ni promoted with Al oxide (Ni-Al/ α -Al₂O₃) and Ni supported over γ -Al₂O₃ obtained from kaolinite (Ni/ γ -Al₂O₃)_k. Data of the dry reforming reaction were obtained employing a sulfur-free gaseous stream so that the operating conditions (CH₄/CO₂=0.5), according to thermodynamic data, the spontaneous deposition of carbon would not occur. The reaction rates were estimated as first order in respect of the methane partial pressure. Once determined that the CH₄ and CO₂ conversions are similar for the different catalysts, it was necessary to know their stability as the conversions on time on stream. The stability of (Ni/ γ -Al₂O₃)_k sample was determined during 25 h at 650 °C and CH₄/CO₂=0.5 ratio. Initially, a slight reduction in the methane conversion was observed for lower reaction time. After 1 h, the conversion was stabilized at 25% (Fig. 1). Previous studies on catalysts of Ni impregnated on commercial alumina [5,6] showed that they suffer important deactivation operating in same reaction conditions.

3.2. Resistance to sulfur poisoning

In order to determine the effect of the presence of sulfur in the feed on the catalysts activity, experimental measure-

Table 2
Catalytic properties of Ni catalyst supported on different solids

Catalysts	$R_{CH_4} \times 10^3$ (mol/g seg)	$X_{CH_4}^a$	$X_{CO_2}^a$
Ni/ α -Al ₂ O ₃	5.02	0.253	0.37
Ni-Al/ α -Al ₂ O ₃	8.13	0.4	0.5
(Ni/ γ -Al ₂ O ₃) _k	5.08	0.25	0.57

Reaction conditions: p_{CH_4} =0.03 atm, CH₄/CO₂=0.5, temperature=650 °C, t_R =0.8×10^{–2} seg.

^a Conversion after 2 h in reaction, (Al₂O₃)_k: support obtained from kaolinite.

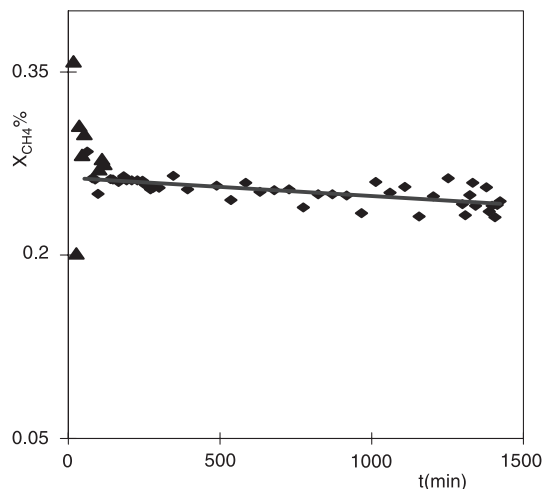


Fig. 1. Methane combustion vs. time on stream on $(\text{Ni}/\gamma\text{-Al}_2\text{O}_3)_k$ catalyst. Reaction conditions: $\text{CH}_4/\text{CO}_2=0.5$, temperature: 650°C , $t_R=0.6\times 10^{-4}/\text{min}$. Methane conversion, \blacklozenge : experience 1; \blacktriangle : repetition experience 1.

ments on the various catalysts were made adding 0.2 ppm of SH_2 to the reactor feed. The experimental data showed that the $(\text{Ni}/\gamma\text{-Al}_2\text{O}_3)_k$ catalyst is the most thioresistant compared with the Al-promoted and -unpromoted Ni catalysts on $\alpha\text{-Al}_2\text{O}_3$. The relative activity, (a), defined as the reaction rate at time t , with respect to initial reaction rate as a function of time on stream is shown in Fig. 2 for the dry reforming of methane at 650°C . The activity curves show that the $(\text{Ni}/\gamma\text{-Al}_2\text{O}_3)_k$ sample present a slight initial deactivation keeping a remanent activity about 90% of initial methane conversion.

On the other hand, the $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ and $\text{Ni-Al}/\alpha\text{-Al}_2\text{O}_3$ catalysts have shown a strong poisoning lowering the methane conversion, after 25 h, about 7% and 5% of the initial activity, respectively. These results are according to our previous works [6,7] about Ni-supported $\alpha\text{-Al}_2\text{O}_3$ catalysts.

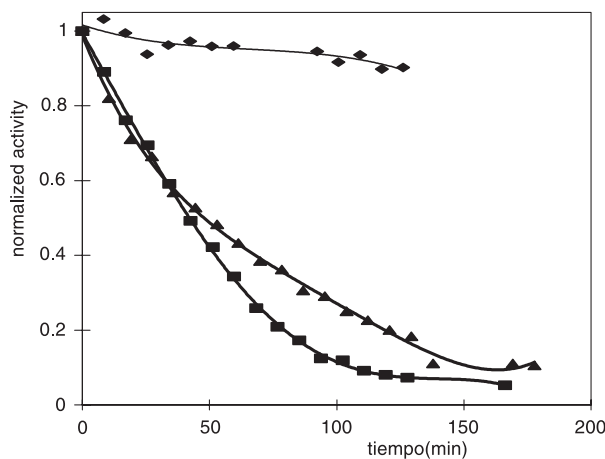


Fig. 2. Normalized activity vs. reaction time at 650°C . References: $(\text{Ni}/\gamma\text{-Al}_2\text{O}_3)_k$ (\blacklozenge), $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ (\blacksquare), $\text{Ni-Al}/\alpha\text{-Al}_2\text{O}_3$ (\blacktriangle). Reaction conditions: $\text{CH}_4/\text{CO}_2=0.5$, temperature: 650°C , $t_R=0.6\times 10^{-4}/\text{min}$.

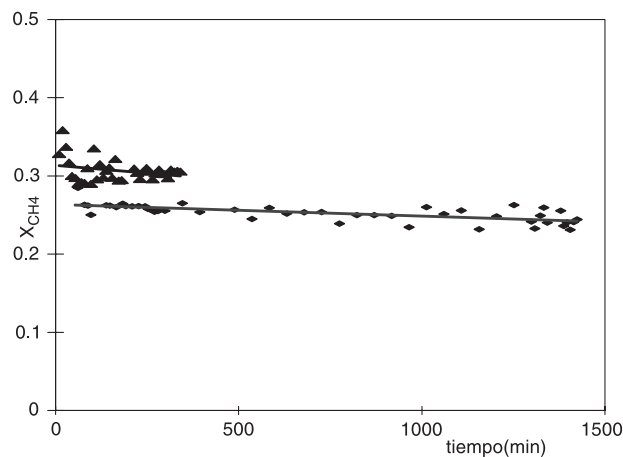


Fig. 3. Methane conversion vs. time on stream on $(\text{Ni}/\gamma\text{-Al}_2\text{O}_3)_k$ catalyst before TPH (\bullet) and after TPH (\blacktriangle). Reaction conditions: $\text{CH}_4/\text{CO}_2=1.3$, temperature: 650°C , $t_R=0.75\times 10^{-4}/\text{min}$.

3.3. Carbon deposition

Knowing that the novel material showed a high resistance to sulfur, $(\text{Ni}/\gamma\text{-Al}_2\text{O}_3)_k$ catalyst was operated under industrial conditions with CH_4/CO_2 ratios near unity, in which spontaneous deposition of carbon is thermodynamically predicted. The different samples were submitted at the dry reforming reaction with an atomic ratio of $\text{CH}_4/\text{CO}_2\approx 1.3$ at 650°C during 25 h. Under these operating conditions the $(\text{Ni}/\gamma\text{-Al}_2\text{O}_3)_k$ present good stability and 90% of methane initial conversion.

After the stability test, the novel catalyst was treated in situ at programmed temperature with in a hydrogen flow (TPH) from T.A. to 900°C to determine the type of carbon formed. TPH pattern of sample in Fig. 3 shows a peak at 760°C ,

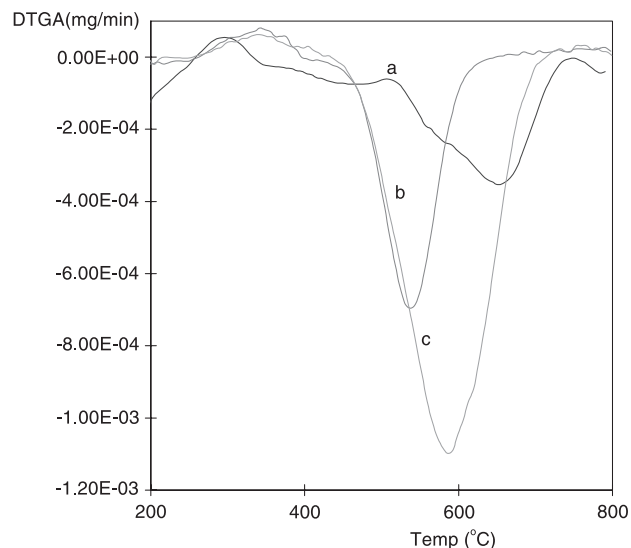


Fig. 4. Derivative of weight variation for the different catalysts, (a) $(\text{Ni}/\gamma\text{-Al}_2\text{O}_3)_k$, (b) $\text{Ni-Al}/\alpha\text{-Al}_2\text{O}_3$, (c) $\text{Ni-Al}/\alpha\text{-Al}_2\text{O}_3$.

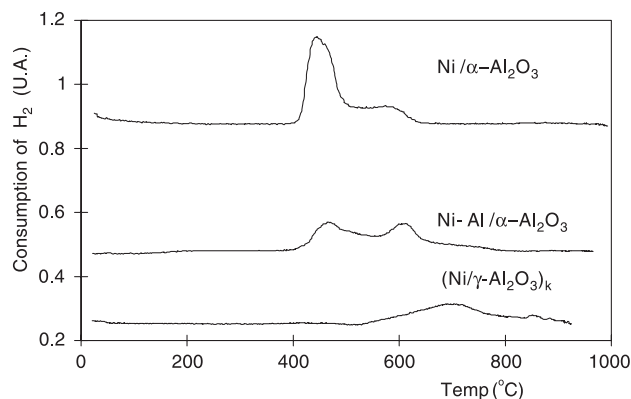


Fig. 5. Temperature-Programmed Reduction patterns of the three catalysts.

which may be identified as filamentous carbon. This carbon species is characteristic of Ni-supported catalysts [7–9].

The sample after hydrogenation was essayed under reforming reaction conditions and higher activity than for fresh sample was observed (Fig. 3). This result suggests that the metallic phase of catalyst was modified during the hydrogenation. The promotional effect of carbon deposition on the methane conversion can be attributed to the Ni surface reconstruction induced by the carbon gasification [11,12].

The amount of carbon deposited on the different catalysts was determined in a thermobalance reactor. Fig. 4 shows DTGA diagrams for the three catalysts. A weight loss of about 2% at 650 °C is observed for (Ni/γ-Al₂O₃)_k (curve a) indicating an inhibition of carbon formation. Meanwhile, the carbon content, determined by TGO, in Al-promoted (curve b) and -unpromoted (curve c) Ni/α-Al₂O₃ catalysts were about 3% and 8%, respectively.

In order to analyse the effect of H₂ and O₂ gases on the catalysts regeneration, a (Ni/γ-Al₂O₃)_k-coked sample was treated with O₂ in the reactor and the catalytic activity at 650 °C was determined not only prior to this sequence but also after it. The fresh catalyst shown a methane conversion equal to 40%. After the elimination of carbon with oxygen, the catalyst reduced at 650 °C during 1 h was active but the methane conversion lowering 28% than in fresh catalyst. It is different than the catalyst regenerated with hydrogen, as was explain before.

The behaviour of the catalyst submitted to TGO experiment may be explained by Ni oxidation during the regeneration that conduce to the diffusion of Ni²⁺ in the alumine structure and formation of Ni–Al spinel, which is not easy to reduce in the catalytic test conditions. The studies about the catalysts regeneration are very important for industrial catalysts.

3.4. Catalysts characterization

In order to correlate the catalytic properties with the active phase, the three samples were characterized by TPR. Fig. 5 shows the thermograms of (Ni/γ-Al₂O₃)_k, Ni-Al/α-Al₂O₃ and Ni/α-Al₂O₃ catalysts. The catalysts supported over α-

Al₂O₃ present two peaks at 470 and 615 °C corresponding to Ni with different interaction with the support. According with the possibility of metal–support interactions, the Ni/α-Al₂O₃ catalyst show the higher Ni reducible amount at lower temperature. On the other hand, the new catalyst, (Ni/γ-Al₂O₃)_k, presents a peak at 700 °C indicating a strong Ni–support interaction. The interaction can contribute to a higher Ni dispersion and affect the carbon deposition. Chen and Ren [10] reported that the carbon deposition is enormously inhibited for the NiAl₂O₄-formation. The strong interaction of NiO bonds in the NiAl₂O₄ contributes to produce smaller crystallites in the catalyst surface and assist to the resistance of the catalysts to sintering and carbon deposition.

4. Conclusions

- The novel support obtained from kaolinite was appropriated to prepare a catalyst that showed a better activity and stability for the dry reforming reaction at 650 °C than the conventional catalyst of Ni/α-Al₂O₃.
- This support gives a high resistance to the sulfur poisoning and carbon deposition to the Ni-supported catalyst in relation with the α-alumine.
- Regeneration by hydrogen of (Ni/γ-Al₂O₃)_k catalyst increases the methane conversion, meanwhile, the treatment with oxygen decreases its catalytic activity. This last behaviour could be due to the spinel Ni–Al, which is not easy to reduce.

5. Uncited reference

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