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Carbon dioxide reforming of methane over K-modified Ni-Al_2O_3 catalysts. Effect of the potassium content

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ABSTRACT

The influence of the potassium content on the performance of a Ni-Al_2O_3 catalyst, prepared by a sol–gel method, in the CO_2 reforming of methane was studied. For this purpose, catalytic activity and resistance to carbon deposition were measured. The characterization techniques used were BET surface area, X-ray diffraction, Transmission Electron Microscopy (TEM), Temperature-Programmed Reduction (TPR) and Temperature-Programmed Oxidation (TPO). The CO_2 reforming of methane was carried out at 750ºC and at a CO_2/CH_4 ratio of 1. K-modified catalysts were prepared by incipient wetness impregnation. The effects of K addition on the physicochemical properties were studied at different potassium contents, from 0 to 1 wt.% K. Compared to the unmodified catalyst, the introduction of K showed constant but slightly less activity, a lowering in the hydrogen yield and a lower carbon deposition after the same operation period. Our results showed the highest increase in resistance to carbon accumulation at a K load of 0.5 wt.%.

KEYWORDS

Methane dry reforming;
Hydrogen and CO;
K-modified Ni-Al_2O_3 catalyst;
Carbon accumulation.

INTRODUCTION

The catalytic dry reforming of methane (DRM) to synthesis gas as a way to produce hydrogen running according to equation (1) has become a promising approach to the utilization of greenhouse gases[1]. It also constitutes an interesting route to process renewable energy sources such as biogas to synthesis gas.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (1)$$

The most important side reactions that are normally present during the process are

$$CO_2 + H_2 \rightarrow CO + H_2O$$

reverse water-gas shift (RWGS) (2)

$$CH_4 \rightarrow C + 2\,H_2 \text{ methane cracking} \qquad (3)$$

$$2\,CO \rightarrow C + CO_2 \text{ Boudouard reaction} \qquad (4)$$

The low H_2/CO ratio obtained is of particular interest in the synthesis of valuable oxygenated derivatives and higher hydrocarbons. A large number of supported catalysts, mainly involving elements of the group VIII, with promising catalytic activity have been proposed for methane reforming. Due to its availability and cost, nickel is preferred from the industrial point of view. The high temperature required for the endothermic reforming reaction makes nickel more susceptible to coking than noble metals. For this reason the development of stable and coke-resistant nickel-based catalysts has been the focus of many studies on the subject. Research on the nature of the support, the preparation of the support and the catalyst, the use of additives and promoters and the amount used has preferentially attracted the attention of many authors, which has been reflected in the open literature[2-14,19].

In a previous paper, the effect of the addition of the metals K, Ca, Mn, and Sn to a Ni-Al_2O_3 catalyst obtained via sol-gel was studied[15]. The catalyst preparation method was based on the use of nickel and aluminum organometallic precursors and a severe pretreatment of the catalyst precursor to obtain high metallic dispersion and high resistance to sintering. The unmodified catalyst proved to be very active, selective and stable in the methane dry reforming reaction[16]. In this paper, the effect of the addition of variable potassium amounts to the same catalyst used before in the DRM reaction both on reforming reactivity and resistance toward carbon deposition was studied.

EXPERIMENTAL SECTION

Catalyst preparation

The unmodified catalyst was prepared by a sol-gel method, details of the technique can be found elsewhere[15]. Basically, aluminum sec-butoxide and nickel 1-methoxy-2-propoxide were hydrolyzed and, subsequently, an acid peptization with HNO_3 was performed. Afterwards, the colloidal solution obtained was concentrated and vacuum-dried, and left to gel in air. The resulting material was dried overnight at 100ºC and calcined in air at 850ºC for 10 h. The severe calcination pretreatment produces a high metal-support interaction forming a spinel of nickel aluminate that, after reduction, markedly suppresses carbon deposition[17]. A nominal nickel content of 14% was utilized. Potassium was incorporated by using incipient wetness impregnation with a KNO_3 aqueous solution to obtain samples with a potassium content of 0.0, 0.25, 0.5, 0.75 and 1 wt.%. The impregnated samples, as well as the unmodified catalyst, were dried overnight at 110ºC and calcined in air at 850ºC for 12 h.

Catalyst characterization

The BET surface area of the catalyst samples was measured using a ChemBet 3000 model Quantachrome sorptometer. The crystalline phases were determined through XRD by means of a Rigaku Geigerflex diffractometer equipped with a graphite monochromator using Cu-Kα radiation. When possible, the nickel crystallite size was calculated using the Ni(111) reflection and the Scherrer formula corrected for instrumental line broadening.

The catalyst reduction behavior was studied by temperature-programmed reduction (TPR). A flow of hydrogen (5% H_2/N_2) of 30 ml min^{-1} and a linear increase in temperature from room temperature to 850ºC at a heating rate of 10ºC min^{-1} were adopted.

The amount of carbon deposited on the catalysts was determined by temperature-programmed oxidation (TPO) using a Shimadzu TGA-51 thermobalance in an air atmosphere at a heating rate of 10ºC min^{-1} from room temperature to 1000ºC.

The surface morphology and crystallinity of the reduced and used catalysts were investigated by using the transmission electron microscopy (TEM) in a JEOL 100 CX system, with a high tension voltage of 100 kV and a magnification of 80000 X. Particle size distribution was obtained to calculate the mean particle sizes.

Catalyst testing

Reforming reactivity studies in DRM were carried out in a fixed-bed flow reactor. Details of the setup and method were given earlier[15]. A catalyst sample of 0.1 g diluted (1/20 wt) with same-sized inert alpha alumina was used. Before reaction, the catalysts were reduced in situ at 850ºC for 14 h under flowing H_2 (30 ml/min) and then cooled down to reaction temperature switching from H_2 to the reaction mixture.

Samples were taken at intervals of 30 min. On-line analysis of the reaction stream was performed by a GC equipped with a 2 m Carbosphere column and using argon as carrier gas. The analytical system was connected to a TCD detector. The data were processed with a Spectra-Physics 4600 Integrator. The CO_2 reforming of methane was carried out at 750ºC, CH_4/CO_2 =1, W/F^o_{CH4} = 0.5 g h mol^{-1} and 0.1 MPa. The yields of H_2 and CO were calculated from the concentration measured by GC as yield of H_2 (%) = 100 x (moles H_{2out}/2 x moles CH_{4in}) and yield of CO (%) = 100 x (moles CO_{out}/ (moles CH_{4in} + moles CO_{2in})).

RESULTS AND DISCUSSION

Characterization

The catalyst specific surface areas are shown in TABLE 1. The addition of potassium produces a certain reduction in the area. After 30 h of operation, the used catalysts show a decrease in the surface area.

TABLE 1 : Catalyst surface area

Catalyst	Catalyst designation	Surface area (m^2g^{-1}) Fresh catalyst	Surface area (m^2g^{-1}) Used catalyst
14%Ni-Al_2O_3	Ni-0K	209	139
14%Ni-0.25%K-Al_2O_3	Ni-0.25K	200	135
14%Ni-0.5%K-Al_2O_3	Ni-0.5K	192	142
14%Ni-0.75%K-Al_2O_3	Ni-0.75K	185	145
14%Ni-1%K-Al_2O_3	Ni-1K	190	140

XRD patterns of all the catalysts showed, for the fresh unreduced catalysts, that: i) the overlapping of the reflections of $NiAl_2O_4$ and γ-Al_2O_3 makes it difficult to distinguish between both phases, ii) NiO characteristic peak is not observed, probably due to the high calcination temperature developed. It can be inferred from this that Ni is preferentially under the form of nickel aluminate spinel in agreement with TPR results, and iii) K_2O characteristic peaks are not present, probably due to the low load of the modifier.

For the reduced samples metallic nickel peaks appear. Finally, for the used samples the line of carbon is not observed, although its presence was detected in the TPO experiments and in the TEM micrographs. Examples of these observations can be seen in reference[15].

For the Ni-0K catalyst, particle sizes, estimated through XRD line broadening, showed an increase in the particle diameter after 30 h on stream from 5.9 nm for the reduced sample to 7.9 nm for the used sample. In the case of the Ni-0.5K catalyst, a particle diameter of approx. 7 nm was observed for the reduced sample and the particle diameter change for the used sample was negligible.

The TPR curves of the fresh catalysts showed a unique band as a broad reduction feature between 590 and 900ºC with a maximum located at about 825ºC for Ni-0K and Ni-0.25K, at about 800ºC for Ni-0.5K, at about 790ºC for Ni-0.75K, and at 775ºC for Ni-1K. The broad reduction feature corresponds to nickel compounds resulting from a very strong metal-support interaction. A sample of pure NiO reduced under the same conditions shows a unique peak with a maximum at about 390ºC, while a $NiAl_2O_4$ sample, also reduced under the same conditions, shows a unique peak with a maximum at about 820ºC. Compared with the Ni-0K catalyst, the Ni-0.5K, Ni-0.75K and Ni-1K catalysts show an improvement in the reducibility through a displacement of the reduction curve maximum of about 25, 35 and 40ºC, respectively. In this case, it seems that potassium modifies the interaction of nickel with alumina, and consequently the reducibility of nickel species.

Catalytic activity, carbon deposition and used catalyst characterization

Figures 1 and 2 illustrate the time on stream dependence of the conversion of CH_4 and CO_2 at 750ºC in the DRM reaction. The conversion of CO_2 was always higher than the corresponding conversion of CH_4, probably due to the influence of the secondary RWGS reaction.

All catalysts showed an initial step of about 5-7 h increase in both conversions, reaching significant stability up to 30 h of operation without significant deactivation. Hence, the activity of the nickel sites is not affected by the accumulation of carbon. This behavior

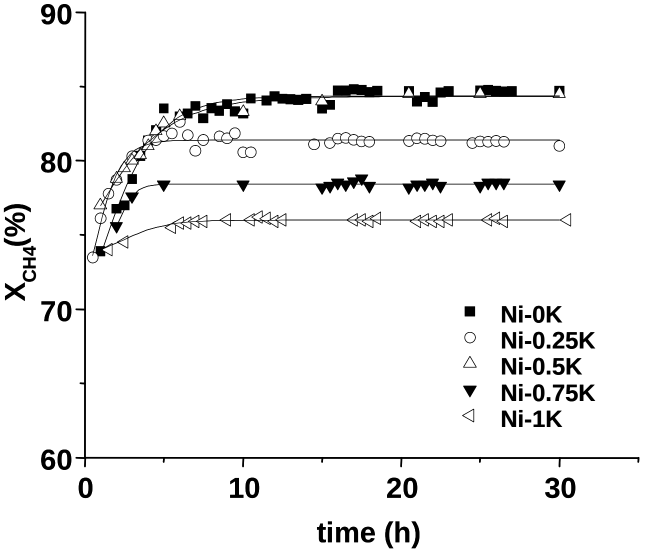

Figure 1 : CH_4 conversion with time on stream, at 750ºC (30 h of reaction).

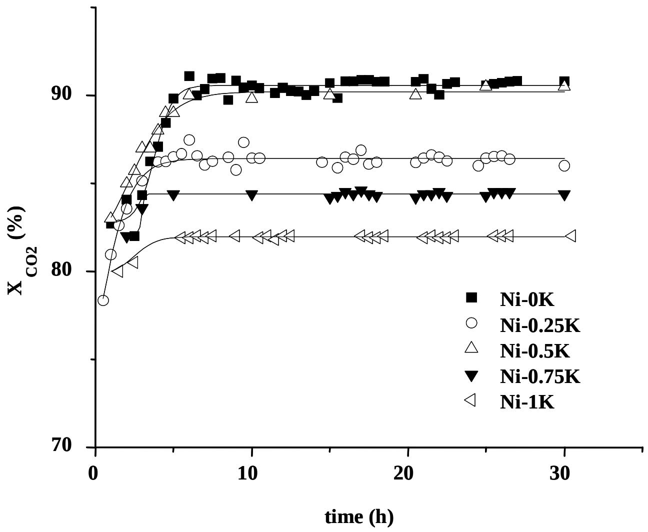

Figure 2 : CO_2 conversion with time on stream, at 750ºC (30 h of reaction).

has been observed when a filamentous carbon structure is formed. In our experiments, the main type of carbon is filamentous carbon as can be seen in the TEM micrographs of reference[15]. According to the growth mechanism of the filamentous carbon with nickel particles at the extremity of carbon filaments, the catalytic activity remains constant as far as the nickel particles are still accessible to reactants.

TABLE 2 shows the data of catalytic activity at 750ºC for the various samples studied, expressed as methane and carbon dioxide stable conversion data, and the total amount of carbon formed (in mg of carbon per gram of catalyst), after 30 h on stream. A decrease in the conversion of both CH_4 and CO_2 with the amount of potassium in the catalysts is observed. Methane conversion decreases from 84% (near the thermodynamic equilibrium at 750ºC for the unmodified catalyst (Ni-0K)) to 76% for the sample with 1% K content (Ni-1K).

The addition of a small amount of potassium has an important effect in reducing the amount of deposited carbon, from 60 mg C/g cat. for the unmodified catalyst to less than 10 mg C/g cat. for the Ni-0.5K sample (TABLE 2). However, higher potassium content seems to be less effective. We found an optimum potassium content of 0.5 wt.% K that leads to a catalyst with 87% reduction in coke deposition and 8% decrease in the catalytic activity, after 30 h on stream.

TABLE 2 : Experimental catalytic activity. Data after 30 h on stream

Catalyst	X_{CH4} %	X_{CO2} %	Y_{H2} %	Y_{CO} %	H_2/CO	Carbon mg C/g_{cat}
Ni-0K	84.	90.8	84	87	0.97	60
Ni-0.25K	84.2	90.1	83.4	86	0.97	60
Ni-0.5K	81,3	86.6	72	91	0.79	8
Ni-0.75K	78	84	64	92	0.69	30
Ni-1K	76	82	57	95	0.60	20

Reaction conditions: 750ºC; CO_2/CH_4: 1.0, W/F^o_{CH4} = 0.5 ghmol^{-1}

Calculations by large-scale density functional theory (DFT) reported by Bengaard et al.[20] showed that potassium added as activity modifier of nickel-based catalysts is deposited mainly on the stepped nickel surface of higher activity for hydrocarbon reforming and carbon formation reactions than the nickel surface with close-packed terraces. This location produces a partial blocking of the most active sites displacing the reforming reaction to the less active, unblocked sites, of the surface with close-packed terraces. As a result, the catalytic activity, as well as carbon deposition, is reduced. Also, from experimental observations Snoeck and Froment[19] proposed a rigorous kinetic model for carbon formation from steam/CO_2-reforming mixtures on a nickel catalyst and explained the influence of the potassium content as a strong reduction of the net rate of carbon formation due to a lower value of the lumped forward rate coefficient for the methane cracking reaction, caused by the partial blocking of sites available by potassium present on the nickel surface itself. Moreover, it has been reported that potassium promotes the carbon gasification rate[21,22].

The analysis of the reaction products (H_2 and CO), also shown in TABLE 2, for H_2 and CO yield and H_2/CO molar ratio, reveals that the presence of potassium produces a decrease in the values of H_2 yield and an increase in the values of CO yield. These results are consistent with the two effects of potassium mentioned above: the blockage of Ni active sites for methane cracking ($CH_4 = C + 2 H_2$) and the enhancement of carbon gasification ($2 CO = CO_2 + C$). Also, observed values of the H_2/CO molar ratio lower than 1 can be explained by the occurrence of the reverse water-gas shift reaction (2), which becomes important at high abundance of CO_2 producing consumption of H_2 and an increase in CO. Carbon accumulation can also occur together with hydrogen, diminishing the H_2/CO molar ratio.

The values of carbon deposition observed for the samples with increasing potassium content can be attributed to the fact that the rate of carbon deposition may not be constant with time. To investigate the rate of carbon deposition, the carbon accumulated after 15 h on stream for the catalysts Ni-0K, Ni-0.5K and Ni-1K was measured and the results are shown in TABLE 3. For the sake of comparison, the corresponding carbon accumulated after 30 h on stream is also included as observed and expected values. The expected values were calculated assuming a constant rate of carbon deposition from the 15 h experiments. The order of increasing carbon accumulation was Ni-0K>Ni-0.5K>Ni-1K, as can be anticipated, but the expected carbon accumulation is higher than that observed for Ni-0K as far as the process of carbon accumulation reduces the number of the most active sites for carbon formation, obstructing the cracking of methane and producing less carbon.

TABLE 3 : Carbon accumulation

Catalyst	Carbon at 15 h (mg C/g_{cat})	Carbon at 30 h (mg C/g_{cat})	
		Observed	Expected
Ni-0K	45	60	90
Ni-0.5K	0	7	0
Ni-1K	7	20	14

However, for Ni-0.5K and Ni-1K, the expected carbon accumulation for 30 h on stream is higher than the observed values, probably due to the loss in contact between potassium species, which are mainly on the support, and the nickel particles and the carbon material formed on them. This leads to less restriction for carbon accumulation and a consequent decrease in the extent of the gasification reaction that is catalyzed by potassium. From these results it can be inferred that the carbon accumulation rate is not constant. This observation can explain the behavior of the values of carbon deposition observed for the samples with increasing potassium content.

Our data confirm that the incorporation of potassium hinders the accumulation of carbon on the catalyst surface, increases the reducibility, probably modifying the metal-support interaction, and modifies neither the size nor the structure of the nickel particles.

From the TEM micrographs of the potassium-free and the Ni-0.5K samples after 30 h on stream in the dry reforming reaction, it was possible to determine the corresponding histogram of their particle size distribution which are shown in Figures 3 and 4, respectively. A comparison between them confirms that a lower amount of carbon is deposited on the sample containing potassium (Figure 4). Moreover, the same filamentous nature of the deposited carbon as that of the potassium-free sample can be observed. It was also determined that, in both cases, the mean size of nickel particles is between 5 and 7 nm.

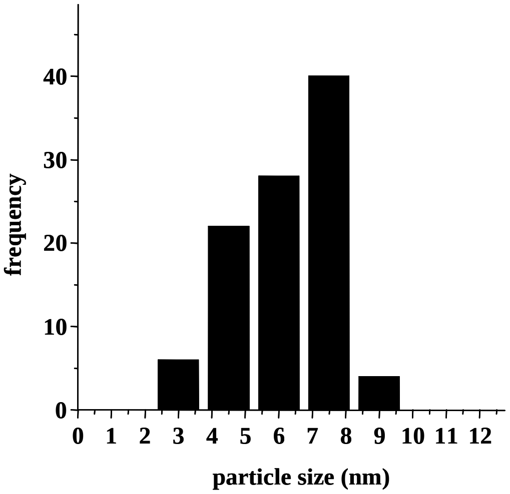

Figure 3 : Histogram of the particle size distribution of used Ni-0K catalyst (after 30 h on stream).

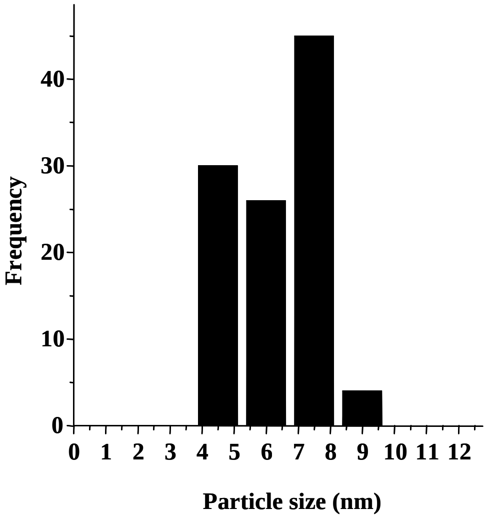

Figure 4 : Histogram of the particle size distribution of used Ni-0.5K catalyst (after 30 h on stream).

These facts indicate that, under our experimental conditions, the modifier decreases neither the amount of carbon deposited without modification in the size nor the structure of the nickel particles. In conclusion, by adding a low amount of potassium (less than 1%), it is possible to obtain a catalyst with a small decrease in activity but with very low carbon deposition. All samples showed the same filamentous nature of the deposited carbon. The amount of deposited carbon on the samples with increasing potassium content showed a minimum at around 0.5 wt.% K.

Other authors have obtained fairly different results; Juan-Juan et al.[18] also observed that the presence of potassium in an impregnated Ni on alumina catalyst in DRM hinders the accumulation of coke on the catalyst surface, but produces a decrease in the catalytic activity. However, they found an optimum potassium content of 0.8 wt.% K that leads to a catalyst with more than 90% reduction in coke deposition and less than 10% decrease in the catalytic activity, after 6 h on stream. It must be considered that their unmodified catalyst produces a high amount of carbon. Moreover, Nandini et al.[23] found that the addition of potassium to a Ni/Al_2O_3 catalyst for DRM decreases the activity at low K contents, but higher loads increase the activity. Also they found that in the K-containing catalyst the amount of coke deposited was low, while noticeable coke coverage on the potassium-free catalyst was observed. Regarding the coke structure, they found that the SEM micrographs of the used catalysts (after 6 h reaction at 700ºC) show a well-defined fibrous conformation on the potassium-free catalyst, while nonstructured coke seems to have been formed on the Ni–K/Al_2O_3 catalyst.

CONCLUSIONS

- A Ni-Al catalyst prepared by sol-gel processing from both Ni and Al organometallic precursors exhibited high activity, remarkable long-term stability and a low amount of carbon accumulation for methane dry reforming.
- In brief, a massive catalyst with a small and homogeneous nickel particle size and no sintering effect was obtained. The severe calcination pretreatment produced a catalyst with high metal-alumina interaction forming a spinel of nickel aluminate, which after reduction markedly suppresses carbon deposition.
- According to our results variable amounts of potassium addition by incipient wetness impregnation leads to catalysts with lower activity than the potassium-free catalyst but with an important reduction in the amount of deposited carbon after 30 h on stream. It seems that the incorporation of potassium produces a partial blocking of the most active sites of the nickel surface for both methane reforming and carbon formation reactions. As a result, the catalytic activity, as well as carbon deposition, is reduced. Also, it is well known that potassium is a good catalyst for carbon gasification.
- An increase in carbon accumulation with a higher potassium content was observed probably due to the fact that the rate of carbon deposition is not constant with time.
- Our data confirm that the incorporation of potassium hinders the accumulation of carbon on the catalyst surface, increases the reducibility, probably modifying the metal-support interaction, and modifies neither the size nor the structure of the nickel particles.
- Our results showed that by adding less than 1% potassium it is possible to obtain a catalyst with a very low carbon deposition. A minimum was observed for the sample with around 0.5 wt.% K after 30 h on stream.

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