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Catalytic Features of Mg Modified Ni/SiO_2/Silica Cloth Systems in the Decomposition of Methane for Making "CO_x-Free" H_2

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Abstract The influence of the Mg addition on the catalytic performance of a 20% Ni based SiO_2/silica cloth system in the decomposition of methane for making "CO_x-free" H_2 in the T_R range 773–873 K has been evaluated. As the Mg_{at}/Ni_{at} ratio increases from 0.10 to 2.20 the incipient Ni–Mg-O interaction becomes stronger until the formation of $Ni_xMg_{(1-x)}O$ solid solution. The presence of Mg^{2+} ions allows a higher carbon capacity (C/Ni, number of CH_4 molecules converted per Ni atom until complete catalyst deactivation) and consequently a higher H_2 productivity of the Ni based systems which results in a smoothing effect of the unavoidable declining activity trend even if it does not affect the tip growth coking mechanism.

Keywords Methane decomposition · "CO_x-free" hydrogen · Thin layer catalysts · Multilayer reactor · Silica cloths

1 Introduction

The development of an efficient catalytic process for the production of "CO_x-free" H_2 for feeding fuel cell systems is greatly desired. A reversible cyclic stepwise process, based on methane decomposition ($CH_4 \leftrightarrows C + 2H_2$, $\Delta H = 75$ kJ mol^{-1}) and carbon removal ($C + O_2 \rightarrow CO_2$, $\Delta H = -341$ kJ mol^{-1}), could represent an interesting way to reach such aim since it appears a direct, mildly endothermic attractive route for producing high purity hydrogen [1–4]. Amongst the various catalytic systems already proposed for the catalytic decomposition of natural gas (CDNG) Ni based catalysts feature high activity at moderate (773–873 K) reaction temperatures (T_R) [5–11]. Previous studies have assessed the structure sensitive nature of the CDNG reaction on Ni systems and the controlling effect of T_R and Ni particle size on coking mechanism [5–7, 11]. Moreover, recent studies of Takenaka et al. have documented the influence of metal-support interaction (MSI) on both catalytic activity and carbon growing mechanism [8], revealing that the filamentous whisker-like coke is formed on Ni catalysts with low MSI, whereas systems with strong MSI give rise mainly to encapsulated coke [8]. Since filamentous coke brings Ni particles on the top, the regeneration of the spent catalyst implies a progressive loss of the active metal which impedes the suitability of Ni systems for any real "CO_x-free" H_2 production process [11]. The addition of MgO to the Ni based catalytic systems and the consequent formation of $Ni_xMg_{(1-x)}O$ solid solution could confer specific features to the Ni active sites [8, 12, 13]. Indeed, the stabilization of small sized Ni crystallites and the higher MSI could favour a *base* growing mechanism of coke deposits [10] which avoids any Ni loss during the regeneration step. This paper is aimed to provide a preliminary evaluation of the textural properties and catalytic features in the CDNG reaction of a series of MgO modified Ni/SiO_2/silica cloths. A complete outline of both activity pattern in the T_R range 773–873 K and regenerability with air of coked systems at 823 K is presented.

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2 Experimental

2.1 Preparation of MgO Modified Ni Thin Layer Catalysts (MxNy-TLCs)

A commercial silica fabric was washcoated with a colloidal SiO_2 solution (Ludox LS, Aldrich product; Surface Area, 215 m^2/g) in order to attain an adequate development of surface area, then SiO_2/silica cloth support was dried at 393 K for 12 h. The weight ratio between SiO_2 and silica cloth was 34/100. A series of MgO modified 20%Ni/SiO_2/silica cloth samples was prepared by co-impregnation of the SiO_2/silica cloth support, shaped in circular form (Φ, 37 mm), with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$. MgO amount was dosed in order to exploit samples with Mg_{at}/Ni_{at} in the range 0.1–2.2. After the impregnation, the samples were dried at 393 K for 12 h and further calcined in air at 873 K for 3 h.

The main physico-chemical properties of MxNy-TLCs are summarized in Table 1.

2.2 Catalyst Testing

The multilayer reactor (MLR) used to perform CDNG tests consists of a quartz tube (Φ_{int}, 39 mm; length, 600 mm) provided at the ends with a metal disc sealed by an O-ring to the quartz tube [11]. Six discs of a MxNy-TLC samples were sandwiched between quartz "spacers" (Φ_{ext}, 37 mm; thickness, 4 mm) and packed into the reactor.

Catalytic tests were carried out at 773, 823 and 873 K and atmospheric pressure using a 10%CH_4/5%N_2/85%Ar (vol/vol) reaction mixture flowing at 250 *stp* mL/min, while catalyst regeneration was performed at 823 K feeding a 5%O_2/95%Ar (vol/vol) mixture (150 *stp* mL/min) through the spent catalytic bed.

The reaction stream was analyzed on-line by an Agilent 3000A micro-GC equipped with two columns (Molecular Sieves 5 Å: film thickness, 12 μm; Φ_{in}, 320 μm; l, 10 m and OV-1: film thickness, 1.2 μm; Φ_{in}, 150 μm; l, 8 m) and two TC detectors. Prior to each run MxNy-TLC samples were reduced "in-situ" at 923 K for 3 h in H_2 flow (150 *stp* mL/min). The catalytic pattern has been evaluated in terms of CH_4 conversion and "carbon capacity" (C/Ni), whereas the *regenerability* of the various catalysts has been evaluated and comparatively accounted by the relative initial activity (α', CH_4 conversion at initial reaction time (t_0) in the cycle i-th divided by CH_4 conversion at t_0 in the first cycle) and relative C/Ni (γ, C/Ni in the cycle i-th divided C/Ni in the first cycle).

2.3 Catalyst Characterization

The Ni and Mg loading were determined by AAS technique using a Perkin Elmer Analyst 200 spectrometer equipped with Ni (λ, 232.0 nm) and Mg (λ, 285.2 nm) lamps. The Temperature Programmed Reduction (*TPR*) measurements in the range 373–1273 K were performed in a continuous flow apparatus using a linear quartz microreactor (i.d., 4 mm) loaded with 40 mg of sample, fed with a 6%H_2/Ar mixture flowing at 60 *stp* mL/min and heated at the rate of 15 K/min. Prior to each run, MxNy-TLC samples were treated "in-situ" at 673 K for 30 min in O_2 flow (30 *stp* mL/min). The O_2 titration method has been adopted to evaluate the reduction degree [14]. Before the O_2 titration, the sample (50 mg) was reduced at 923 K in flowing H_2 (100 *stp* mL/min) and then flushed in He (100 *stp* mL/min) at 923 K for 30 min. The reduction degree of NiO was determined by the O_2 uptake ($V_{O_2} = 0.2$ μL) at 923 K. H_2 uptake and the metal dispersion (D) of the "fresh" catalysts were evaluated by H_2-TPD measurements in the range 193–923 K, after reduction at 773 K for 1 h, assuming the chemisorption stoichiometry H/Ni_{surf} of 1/1 [15]. The surface average Ni particle size ($d_{H_2-TPD}(nm)$) was evaluated on the basis of the equation suggested by Smith et al. [15] assuming a spherical shape of the metal particle:

$$d_{H_2-TPD}(nm) = 101/D(\%)$$

The amount of coke on the "spent" catalysts was determined by CHNS elemental analysis (*Carlo Erba Instrument CHNS-O EA1108*) and TGA/DSC (*Netzsch STA 409 C analyzer*) measurements. The particle size distribution of "fresh" and "used" catalysts was

Table 1 List of Ni based thin layer catalysts and relative physico-chemical properties

Catalyst	Ni loading (%)	Mg loading (%)	Mg_{at}/Ni_{at} ratio	S.A.$_{BET}$ (m^2/g)	MSA (m^2_{Ni}/g)	D_{Ni} (%)	d_s (nm)
N-TLC	19.5	–	–	51.0	3.6	7.1	14.3
M1N9-TLC	17.5	0.9	0.10	44.0	2.6	5.9	17.2
M1N4-TLC	17.3	1.8	0.26	43.7	4.3	9.7	10.4
M1N2-TLC	20.5	4.4	0.46	42.7	5.8	10.8	9.3
M1N1-TLC	18.9	7.8	1.04	56.9	4.8	10.4	9.7
M2N1-TLC	26.9	22.5	2.20	8.9	4.3	5.8	17.5

–, Both SA_{BET} and MSA values are referred to the total weight of the catalyst sample evaluated by Transmission Electron Microscopy (TEM) analysis using a *PHILIPS CM12* instrument provided with a high resolution (HR) camera for acquisition and elaboration of TEM images. Specimens were prepared by ultrasonic dispersion of catalyst samples in isopropyl alcohol, depositing a drop of suspension on carbon supported films. The surface average Ni particle size (d_{TEM}) of fresh and used catalysts was calculated by the following statistical formula:

$$d_{TEM} = \sum n_j d_i^3 \Big/ \sum n_j d_i^2,$$

where n_i and d_i are the number and the diameter of particles, respectively.

3 Results

The results presented in Table 1 indicate that the addition of 1–7 wt% of Mg to the 20%Ni/SiO$_2$/silica cloth catalyst does not affect neither the surface area (S.A.$_{BET}$) nor the Ni dispersion, only for the M2N1-TLC sample (Mg$_{at}$/Ni$_{at}$, 2.20), a significant loss of S.A.$_{BET}$ (8.9 m^2/g) is observed. Such findings allow to rule out any textural promoting effect of MgO until a Mg$_{at}$/Ni$_{at}$ ratio of 1.04. However, the structural rearrangement of the M2N1-TLC catalyst does not imply any significant change in the Metal Surface Area (MSA). This evidence is probatory of the formation of a $Ni_xMg_{(1-x)}O$ solid solution which favours the stabilization of highly dispersed Ni crystallites. TPR profiles of the MxNy-TLC samples are outlined in Fig. 1. When the Mg content rises from 1 to 22 wt% a progressive shift to higher temperatures of both onset temperature of reduction ($T_{o,red}$) and peak maxima (T_{Mi}) in the TPR patterns of the studied systems is observed (Table 2). In addition, the increase of the Mg$_{at}$/Ni$_{at}$ ratio from 0.1 (M1N9-TLC) to 2.2 (M2N1-TLC) causes a progressive lowering of the reduction degree from 1.0 to 0.45, respectively.

In Fig. 2 is outlined the catalytic performance of both bare and MgO modified Ni/SiO$_2$/silica cloth systems in terms of CH$_4$ conversion with time on stream (tos) at 773, 823 and 873 K. The evolution of the CDNG reaction results in the formation of carbon overlayers and/or filamentous carbon entities which cause the progressive catalyst deactivation according to a pattern controlled by the nature and surface features of the catalyst, T_R, loading of active species and mass velocity of the reaction mixture [11].

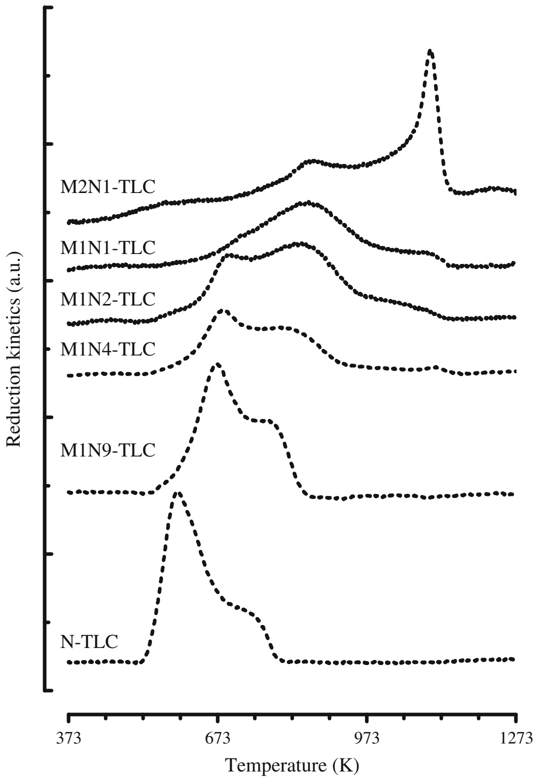


Fig. 1 Temperature programmed reduction (TPR) profiles of Ni–MgO/SiO$_2$/silica cloth catalysts

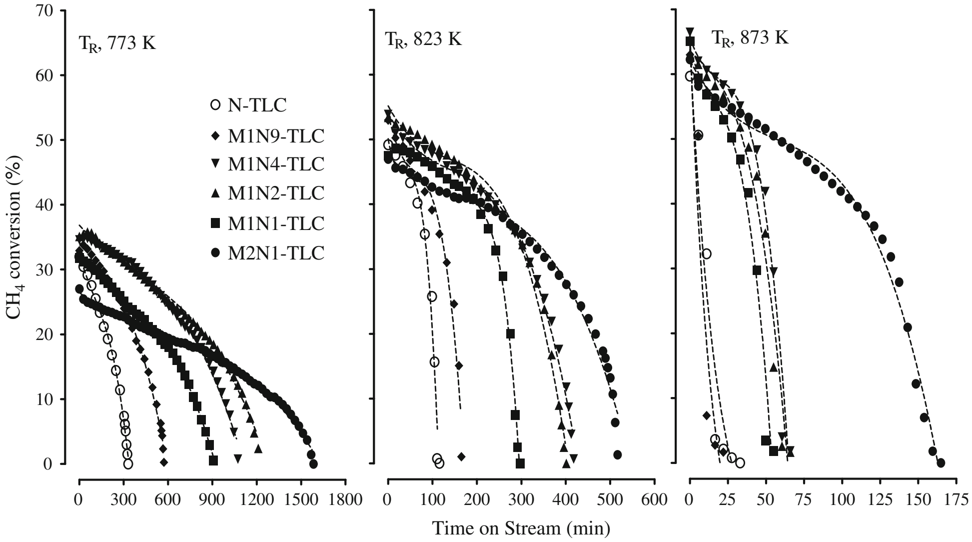
Table 2 TPR of Ni–MgO/SiO$_2$/silica cloth catalysts

Catalyst	$T_{o,red}$ (K)	T_{M1} (K)	T_{M2} (K)	T_{M3} (K)	NiO reduction degree
N-TLC	515	592	739	–	1.00
M1N9-TLC	538	671	783	–	1.00
M1N4-TLC	540	676	815	–	1.00
M1N2-TLC	557	692	831	–	0.86
M1N1-TLC	622	723	844	–	0.75
M2N1-TLC	684	–	855	1023	0.45

Onset temperature of reduction ($T_{o,red}$), temperature of peak maxima (T_{Mi}) and NiO reduction degree

As the T_R rises from 773 to 873 K (Fig. 2) a general increase in the initial CH$_4$ conversion (from 35–40% to 65–70%) along with a general decrease of the catalyst lifetime (from 600–1500 to 25–170 min) has been observed. Any addition of MgO to the Ni/SiO$_2$/silica cloth system (N-TLC) causes a lowering in the initial activity (from 35% to 27%) and an enhancement in the catalyst lifetime. The extent of both effects rises with the Mg$_{at}$/Ni$_{at}$ ratio. Namely, the lifetime of the M2N1-TLC sample at 773 K (1500 min) is 5 times higher than that of the bare N-TLC system in the same operating conditions. However, the most significant activity index in the CDNG catalysts is the C/Ni, then in Fig. 3a the influence of the Mg$_{at}$/Ni$_{at}$ on the C/Ni of the studied catalysts is outlined. The highest C/Ni value at any T_R is associated with the Mg$_{at}$/Ni$_{at}$ ratio of 0.5 (M1N2-TLC). Furthermore, since the reduction degree of NiO of MxNy-TLC samples with Mg$_{at}$/Ni$_{at}$ higher than 0.26 is lower than 1 (Table 2), the carbon capacity values of the catalytic systems have been recalculated taking into account only the reduced fraction of the Ni atoms (C/Ni$_{red}$)

Fig. 2 Catalytic decomposition of natural gas on Ni–MgO/SiO_2/silica cloth systems. Methane conversion vs time on stream at 773, 823 and 873 K



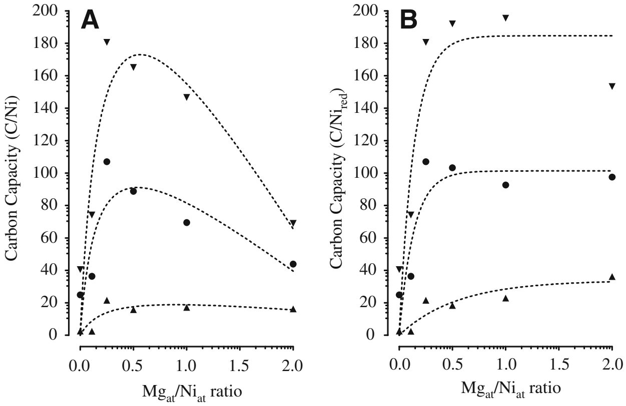


Fig. 3 Catalytic decomposition of natural gas on Ni–MgO/SiO_2/silica cloth systems. Influence of Mg_{at}/Ni_{at} ratio on carbon capacity at 773 (▼), 823 (●) and 873 K (▲) refered to (**a**) total (C/Ni) and (**b**) reduced fraction (C/Ni_{red}) of nickel content

and plotted against the Mg_{at}/Ni_{at} (Fig. 3b). These relationships reveal a saturation-shaped trend with a plateau for Mg_{at}/Ni_{at} ratio higher than 0.5. The carbon capacity values, irrespective of the reduction state of the Ni species, decrease with T_R.

In Fig. 4 are reported the results of a comparative regeneration test of N-TLC and M1N4-TLC catalysts used at 823 K. The sequence of the regeneration runs induces a progressive lowering in both initial activity and lifetime. Such negative effects are much more marked for the N-TLC system. The trends of relative initial activity and relative C/Ni with the sequence of the regeneration runs are shown in Fig. 5. These findings indicate that after 4 runs the bare N-TLC catalyst looses the 50% of the initial activity, while the M1N4-TLC sample undergoes a loss of the initial activity of 20%. The relative carbon capacity for the N-TLC and M1N4-TLC catalysts is depressed with the regeneration runs to the 5% and 20% of the initial value, respectively.

4 Discussion

The introduction of MgO into the formulation of the active phase affects both the surface-structure features and the activity pattern of the 20%Ni/SiO_2/silica cloth catalysts. The modification of the reduction kinetics (Fig. 1), the highly enhanced stability to the sintering phenomena (Table 3), the higher carbon capacity values (Fig. 3) which reflect a higher specific H_2 productivity (mol $H_2 \cdot Ni_{red}^{-1} \cdot s^{-1}$) at any Mg_{at}/Ni_{at} ratio and the higher activity regain after each regeneration run (Fig. 4) along with the lower H_2 productivity loss during the reaction-regeneration sequence (Fig. 5) are clues of the positive effect of the Mg^{2+} ions on the reactivity of the Ni active species. This enhancing effect could be ascribed to a specific Ni–Mg-O interaction which results stronger and much more effective than the Ni–Si-O one. TPR profiles (Fig. 1) and NiO reduction degree of the MxNy-TLC catalyst samples account for the Ni–Mg-O interaction which becomes stronger with the rise of the Mg_{at}/Ni_{at} ratio until the formation of a quasi-ideal $Ni_xMg_{(1-x)}O$ solid solution featured by the extraction-reduction process of isolated Ni^{2+} ions marked by the reduction peak centred at 1023 K (Table 2). The longer run time and consequently the larger area delimited by the methane conversion vs tos curve and the higher C/Ni_{red} values fingerprint an enhanced reactivity of the Ni crystallites ascribable to the "*electron donor*" role of the Mg^{2+} ions in the Ni–Mg-O moieties.

The activity decay of both bare and MgO modified Ni/SiO_2/silica cloth systems becomes steeper with T_R, however the presence of Mg^{2+} ions implies a smoothing effect on such declining activity trend. It can be inferred that the Mg^{2+} ions depress on the kinetics of the activity decay. The extent of such effect rises with the Mg_{at}/Ni_{at} ratio. The M2N1-TLC system, characterized by a prevalent $Ni_xMg_{(1-x)}O$ solid

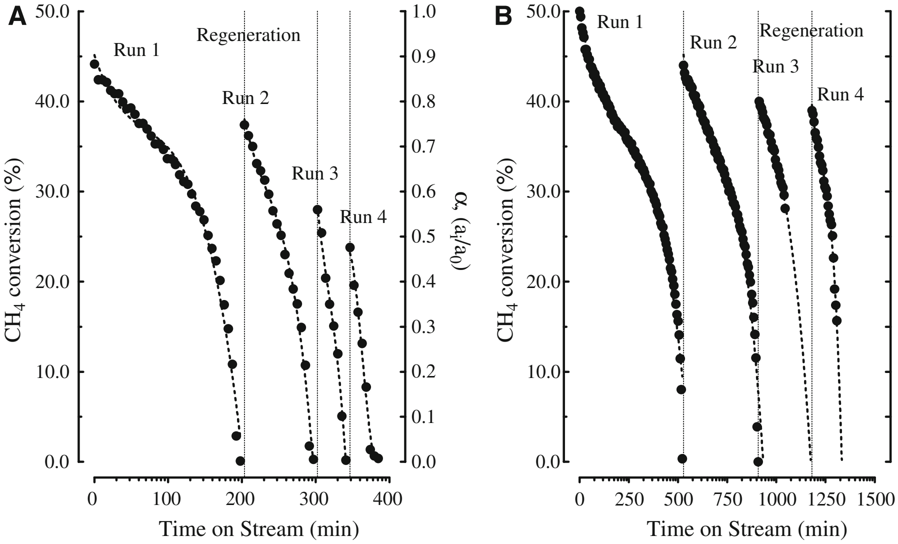


Fig. 4 Catalytic decomposition of natural gas on Ni–MgO/SiO_2/silica cloth systems. Methane conversion vs time on stream of (**a**) N-TLC and (**b**) M1N4-TLC catalysts at 823 K in the sequence of reaction-regeneration test runs. At the end of each run the catalyst undergoes a regeneration treatment with air at 823 K for 3 h

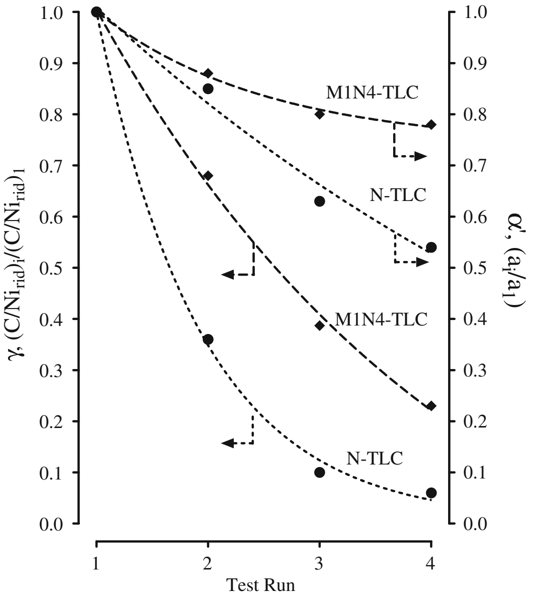


Fig. 5 Catalytic decomposition of natural gas on Ni–MgO/SiO_2/silica cloth systems. Relative activity (α', a_i/a_1) and relative carbon capacity (γ, $(C/Ni_{red})_i/(C/Ni_{red})_1$) of (**a**) N-TLC and (**b**) M1N4-TLC catalysts at 823 K in the sequence of reaction-regeneration test runs. At the end of each run the catalyst undergoes a regeneration treatment with air at 823 K for 3 h

Table 3 Average Ni particle diameter of "fresh" and "used" N-TLC and M1N2-TLC catalysts

Catalyst	d_{H_2-TPD}(nm) Fresh	d_{TEM} (nm) Used at 823 K	d_{TEM} (nm) Used at 873 K
N-TLC	14.3	145.0	445.0
M1N2-TLC	9.3	13.4	17.8

solution, denotes a catalytic pattern which cannot be assimilated neither to that of the bare (N-TLC) nor to those of the Mg modified Ni (M1N9-TLC, M1N4-TLC, M1N2-TLC and M1N1-TLC) systems. The progressive activity decline of the studied catalysts is the consequence of the progressive masking and/or unavailability of the active Ni surface. It can be attributed to the surface coverage by the carbonaceous residues (encapsulating effect) or to the breaking of the filamentous carbon species formed by a tip growth coking mechanism featured by the Ni crystallites on the top of such whisker-like or nanotube carbon structures. The coking mechanism is controlled by both T_R and Ni particle size [5, 11]. At T_R higher than 823 K and for larger Ni crystallites (>60 nm) encapsulating carbon overlayers along with filamentous carbon species are formed [11]. This reaction pattern can be the consequence of the fact that at $T_R > 823$ K the rate of methane decomposition on Ni surface is higher than that of carbon diffusion into the Ni particle resulting in a steeper activity decay due to the sudden inaccessibility of the active Ni surface which appears covered by a continuous film of carbonaceous residues [6, 7, 11].

TEM analysis of "spent" Mg modified Ni/SiO_2/silica cloth catalysts (here not reported for sake of brevity) allows to rule out any significant change in both coking mechanism and factors controlling the formation of the various coke species induced by the presence of Mg^{2+} ions in the formulation of the active phase. The higher C/Ni_{red} values along with the higher relative carbon capacity (γ) and relative activity (α') during the sequence of reaction-regeneration test runs, enabled by the addition of Mg^{2+} ions to the Ni based catalyst, could be the result of concurrent geometric and electronic effects. On this account, it could be inferred that Mg^{2+} ions act as spacers of the Ni crystallites preventing their sintering during the time on stream, while the *electron donor* character of the Mg^{2+} ions could provide Ni active units with an additional electronic charge which improves the efficiency of such sites in the activation of the C–H bond of the CH_4 molecules. However, since the specific activity of Ni sites in bare and Mg modified systems does not change, any electronic effect of the Mg^{2+} ions on the reactivity of the Ni active sites can be ruled out.

The smoothed activity decay of Mg modified catalytic systems is mainly ascribable to the inhibiting effect of the sintering phenomena which generates highly sized Ni crystallites during the reaction at $T_R > 823$ K. The growth of the Ni particle size implies the above invoked encapsulating effect of the active sites. Finally, in spite of the positive effect exerted by the Mg^{2+} ions on the catalytic performance of the Ni based SiO_2/silica cloth catalyst, the decreasing recovery of the initial activity after any regeneration treatment, reflecting a progressive loss of active component likely owing to the detachment of the Ni particles from the surface of the SiO_2 support, leads to disregard the exploitation of the Mg modified Ni based catalysts for a practical application of the CDNG process. On the whole, the above results confirm the need to find novel catalytic systems for the CDNG reaction acting according to a base growth coking mechanism which avoids any loss of the active phase in the reaction-regeneration working cycle [10].

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