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Stability promotion of Ni/α-Al_2O_3 catalysts by tin added via surface organometallic chemistry on metals Application in methane reforming processes

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Abstract

This paper reports the effect of selective tin addition to nickel catalysts via a controlled technique (surface organometallic chemistry on metals, SOMC/M), and the performance of the resulting systems in methane reforming processes: partial oxidation (POM), CO_2 reforming (R) and mixed ($CO_2 + O_2$) reforming (MR), with particular emphasis on their resistance to coke formation. It is demonstrated that SOMC/M techniques allow to obtain well-defined bimetallic phases in a controlled way. It is found that there is a range of tin concentrations (0.01–0.05 wt.%) for which the stability of the bimetallic catalysts is markedly enhanced with respect to nickel catalyst, without affecting either the activity level or the selectivity to syngas. These facts are explained in terms of a more demanding nature in size of the active sites needed for carbon formation reaction, when compared to methane activation reaction to synthesis gas. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Synthesis gas; Methane reforming processes; Tin nickel catalysts; Surface organometallic chemistry

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1. Introduction

The production of syngas from natural gas reforming has gained increased importance for fuel cells, petroleum refining processes (hydrotreating and hydrocracking), petrochemical industry (methanol, ammonia and oxoalcohols), hydrocarbons via Fischer Tropsch, etc. [1–3]. While most syngas is obtained by the traditional methane steam reforming process, some other routes like partial oxidation (POM), CO_2 reforming and mixed reforming ($CO_2 + O_2$) may be more attractive depending on factors such as H_2/CO ratio, product purity and feedstock availability (purity and cost, including oxygen).

Whereas steam and CO_2 reforming reactions are endothermic, requiring large energy input (in general a combustion furnace), POM is exothermic and is more energy efficient. Besides, the absence of the furnace avoids the generation of pollutant gases (NO_x, CO, SO_x and CO_2). Due to the exothermic nature of POM of methane, local hotspots are usually formed [4–6]. CO_2 reforming (R), on the other hand, is an interesting reaction because of the consumption of both reactives (CO_2 and CH_4), which are critical for the greenhouse effect. Besides, in many natural gas fields CO_2 is found together with CH_4. Mixed reforming (MR) appears as a technological alternative to improve the control of

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the temperature, critical for POM reaction, with the possibility of obtaining H_2/CO ratios between 1 and 2.

Ni-based catalytic systems are industrially used in the conventional process of steam reforming. In the case of POM, R and MR reactions, high selectivity to H_2 and CO with excellent methane conversion has been reported on supported transition metal catalyst, particularly Ni catalysts [1,7–12].

In relation to the mechanism of POM reaction, there have been proposed a one-step (or direct transformation) and a two-step mechanisms [8,13,14]. This last one consists of a first step in which the total combustion of part of the methane occurs and a second step in which the remaining methane reacts with the combustion products in a classical reforming. For R reaction, a mechanism involving dissociation of CO_2 and CH_4 is suggested [14–17].

The analysis of the stability of the active phase is a very important subject related to POM, R and MR processes, because operating conditions are thermodynamically favorable to carbon formation (temperatures above 600°C, low O/C and H/C ratios) and sintering of Ni particles (high temperatures, presence of steam) [1,18–22]. With respect to the deactivation by sintering, several contributions mentioned in literature denote the effect of the nature of the support and/or the use of promoters to inhibit this mechanism.

The deactivation by coke formation on Ni-based catalysts is surely the most important deactivation mechanism in the processes of methane transformation to syngas. To suppress carbon deposition, several strategies have been proposed. The use of supports having basic properties (CaO, MgO, La_2O_3) notably improves the resistance to coke formation due to the gasification of superficial carbon species [15,23,24].

Industry employs partly sulfur-poisoned nickel catalysts [25], taking advantage of the fact that the dissociation of CH_4 is influenced by the nature of the ensembles of the active sites, in order to strongly diminish the rate of carbon formation. Similar effects to those obtained with sulfur, could be obtained alloying nickel with copper. When copper concentration is small, it is observed an increase in the rate of carbon formation and for $\mathrm{Cu/Ni} > 0.10$ this rate decreases, but it is not possible to eliminate carbon formation [17]. As it can be seen, the development of new stable supported nickel catalysts is of great interest due to their practical application in methane conversion processes.

Tin is recognized as stability promoter against coke formation in many processes, like paraffin dehydrogenation and naphtha aromatization [26]. Recently, the important effect of tin addition has been demonstrated toward stability promotion in syngas obtention by CO_2 R process using PtSn catalysts [27]. In the case of Ni-based catalysts, very few literature citations are found in relation to the effect of tin addition. Choi et al. [28], working with SnNi catalysts (atomic ratio $\mathrm{Sn/Ni} \sim 0.05$) prepared by impregnation of $SnCl_2$ and an inorganic Ni precursor, found that the activity of the catalyst was very low in the CO_2 R reaction, indicating a poisoning effect of Sn over Ni.

In this paper, we report the effect of selective tin addition on nickel catalysts via a controlled technique, surface organometallic chemistry on metals (SOMC/M), on their performance in POM, R and MR reactions, with particular emphasis on the resistance to coke formation. The preparation technique employed leads to a specific reaction of tin with supported transition metals, as it was previously demonstrated [29].

2. Experimental

The supported Ni catalysts with a content of 2% (w/w) Ni were prepared by impregnation of Ni–acetylacetonate as precursor compound in a benzenic solution at 60°C. The support employed was α-Al_2O_3 prepared in the laboratory according to Marturano et al. [30], modified by impregnation with $Al(NO_3)_3\cdot 9H_2O$, so as to obtain 1% (w/w) Al in the solid ($S_g = 10.5\,m^2\,g^{-1}$, $V_p = 0.21\,cm^3\,g^{-1}$). The support was calcined in air at 600°C before use. After the impregnation step, the solids were dried at 120°C for 2 h and then calcined in flowing air at 750°C for 4 h.

Tin modified systems were prepared by reaction between Ni catalysts (pre-reduced during 2 h in flowing H_2 at 700°C) and a solution of $SnBu_4$ in *n*-heptane at 90°C under flowing H_2. The solids obtained after this procedure could still have some butyl groups grafted to the surface. Then, they were washed several times with *n*-heptane at room temperature and dried in flowing Ar at 100°C for 2 h. The bimetallic catalysts (SnNi) were finally obtained by activation in flowing H_2 at 500°C. The contents of tin were in the range 0–0.1, expressed as $\mathrm{Sn/Ni^{bulk}}$ atomic ratio. The size distribution of metallic particles was determined by transmission electron microscopy (TEM) using a Jeol 2010 instrument. To estimate the mean particle size (d_{av}), the particles were considered spherical and the second moment of the distribution was employed. Temperature-programmed reduction (TPR) of the catalysts was performed by means of a conventional equipment using a programmable furnace and the response was measured using a thermal conductivity detector. The composition of the feed flow was $H_2/N_2 = 1/9$ and the heating rate was 10°C min^{-1} from room temperature to 1000°C.

The operating conditions for catalytic tests were atmospheric pressure, temperature between 500 and 900°C, and the following feed compositions: for POM, $N_2/CH_4/O_2 = 11/2/1$; for R, $N_2/CH_4/CO_2 = 6/1/1$ and for MR, $N_2/CH_4/O_2/CO_2 = 22/4/1.5/1$. For all the studied reactions, the ratio $O/C = 1$ and approximately the same p_{CH_4}; for MR reaction the feed composition was chosen so as to obtain autothermal conditions. The stability was evaluated in terms of an activity coefficient a_{CH_4}, which is the ratio between the rate value of CH_4 consumption corresponding to t h on stream and the initial value. Catalysts were analyzed in a thermogravimetric equipment (Shimadzu TG-50), measuring weight variation as a function of time, employing different feed flow compositions: He/CH_4, $He/CH_4/O_2$, $He/CH_4/CO_2$. Carbon deposits produced were quantified and characterized by temperature-programmed oxidation (TPO/TGA). Samples of 0.010 g were analyzed, feeding with air at a flow-rate of 40 cm^3 min^{-1}, and a heating program of 10°C min^{-1} from room temperature to 850°C.

3. Results and discussion

Table 1 shows the characteristics of SnNi samples prepared by reaction between $SnBu_4$ and Ni/α-Al_2O_3 using techniques derived from SOMC/M, which permit to obtain bimetallic catalysts with variable composition in a controlled way. Catalysts with very low Sn/Ni^{bulk} atomic ratios are obtained from Sn concentrations varying between 0 and 0.4 wt.% on supported Ni (2 wt.% Ni). The Sn/Ni^{surface} atomic ratio column arises from considering the dispersion values estimated from the Ni mean particle size determined by TEM for Ni/α-Al_2O_3 and from the application of the expression proposed by Brunelle et al. [31]. TEM results show that the mean particle sizes (d_{av}) for SnNi samples are slightly higher than the ones of the monometallic catalyst, and this would be in agreement with a specific interaction between nickel and tin.

Fig. 1 presents TPR results, noticing that for nickel monometallic catalyst, a principal peak of hydrogen consumption appears at about 610°C; this temperature is higher than the one corresponding to the reduction of bulk NiO that occurs at around 300°C. This is in agreement with a strong interaction between the nickel precursor and the α-Al_2O_3 support modified by a layer of aluminum oxide [32]. In the case of SnNi systems, all bimetallic catalysts present a principal peak of hydrogen consumption between 480 and 500°C, as can be seen in Fig. 1. The temperature decrease of the order of 100°C may be assigned to a modification in the interaction between nickel oxide and the support as consequence of a close relation

Table 1
Composition and characteristics of the employed catalysts

Catalyst	Ni (wt.%)[a]	Sn (wt.%)[a]	d_{av} (nm)[b]	Sn/Ni^{bulk} [c]	Sn/Ni^{surface} [c]	H_2 [d]	R (%)[e]
Ni	2	0	16.7	0	0	290	85
SnNi 003	2	0.012	17.5	0.003	0.06	329	96
SnNi 005	2	0.02	ND[f]	0.005	0.1	317	92
SnNi 01	2	0.04	ND[f]	0.01	0.2	344	99
SnNi 025	2	0.1	ND[f]	0.025	0.5	350	98
SnNi 05	2	0.2	18.5	0.05	1.0	378	100
SnNi 1	2	0.4	ND[f]	0.1	2.0	ND[f]	ND[f]

[a] Measured by atomic absorption.

[b] Mean particle size, measured by TEM.

[c] Expressed as atomic ratio.

[d] H_2 consumption (μmol g^{-1}) determined by TPR (for conditions, see the text).

[e] Reduction degree estimated by [(amount of H_2 consumption by TPR)/(theoretical amount of H_2 consumption for total reduction)] × 100.

[f] Not determined.

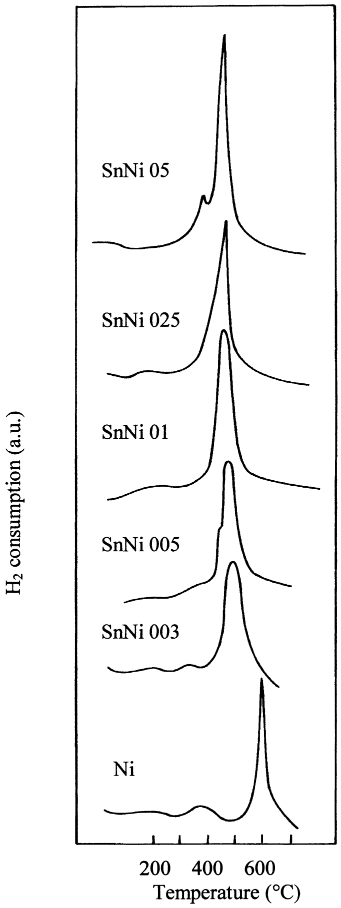

Fig. 1. TPR profiles for the bimetallic SnNi and Ni studied catalysts.

between the corresponding nickel and tin oxides. These results are in agreement with the ones obtained by TEM. The higher hydrogen consumption observed in Table 1 for bimetallic catalysts, derived from TPR experiments, are compatible with the total SnO_2 reduction that occurs below the reduction temperature of bulk SnO_2 (approximately 700°C) [33]. This also indicates a strong intimacy between both metals: the H_2 dissociation is produced on Ni particles and then the atomic hydrogen reduces the SnO_2.

Table 2 shows the catalytic performances of the systems studied in this work for POM and R reactions, measured after 1 h on stream. In these experiments, where the samples were pre-reduced in hydrogen flow at 700°C, it is observed that small Sn amounts of about 0.04 wt.% (SnNi 01) do not appreciably affect the catalytic activity. From this value up, as the tin content increases, the activity decreases, and, for ratios of the order of SnNi 025 sample or higher, a very important poisoning effect of tin is evidenced on the catalytic activity.

Table 2

Results of catalytic activity tests performed at 700°C, methane conversion (X_{CH_4}%) measured after 1 h on stream (for experimental conditions, see the text)

Catalyst	POM		R	
	X_{CH_4}%	H_2/CO	X_{CH_4}%	H_2/CO
Ni	85	2.5	70	0.8
SnNi 003	84	2.5	73	0.9
SnNi 005	70	2.2	72	1.0
SnNi 01	68	2.6	67	1.0
SnNi 025	5	ND[a]	10	ND[a]
SnNi 05	4	ND[a]	3	ND[a]
SnNi 1	4	ND[a]	3	ND[a]

[a] Not determined.

All pre-reduced catalysts were submitted to TGA, feeding the samples with a mixture of $He/CH_4 = 2/1$, varying the temperature from room temperature to 900°C. The diagrams presented a weight increase produced by the carbon deposition originated in the methane cracking ($CH_4 \rightarrow C + 2H_2$). These assays give evidence of the activation of the methane molecule on the catalytic active phase, which in the case of active catalysts for the R reactions, takes place at temperatures around 600°C. For samples containing higher tin concentrations ($Sn/Ni^{bulk} > 0.025$), the thermogravimetric diagrams showed no weight variation as a function of the temperature, because the bimetallic phase formed is not able to activate the methane molecule. These results are in agreement with the ones of the reforming activity shown in Table 2, demonstrating the poisoning effect of Sn.

Conversion and selectivity results (H_2/CO ratio) for POM, R and MR reactions are presented in Table 3. These data correspond to the two catalysts with the highest activity levels, the monometallic Ni and the bimetallic SnNi 003, pre-reduced in both cases, measured at 1 h on stream.

The H_2/CO ratio was slightly higher than 2 for POM, near to 1 for R and variable between 1 and 2 for MR. The possibility of controlling the H_2/CO ratio obtained from the R reaction is a very impor-

Table 3
Conversion of CH_4 and selectivity (measured as H_2/CO ratio) for pre-reduced Ni and SnNi 003 catalysts, submitted to POM, R and MR reactions (for experimental conditions, see the text)

Temperature (°C)	Reaction	Ni		SnNi 003	
		X_{CH_4}%	H_2/CO	X_{CH_4}%	H_2/CO
650	POM	78	2.6	77	2.6
	R	56	0.8	55	0.9
	MR	42	1.5	48	1.5
700	POM	85	2.5	84	2.5
	R	69	0.8	73	0.8
	MR	60	1.4	64	1.4
750	POM	88	2.2	91	2.1
	R	83	1.0	90	1.0
	MR	76	1.4	80	1.4

tant characteristic taking into account the subsequent application of the synthesis gas obtained. The catalytic activity measured through conversion of CH_4 (X_{CH_4}%) follows the order POM > R ≈ MR for Ni catalyst as well as for SnNi bimetallic catalysts.

When fresh catalysts are placed in the reactor in an oxidized state, after the calcination step, Ni and SnNi catalysts ($Sn/Ni^{bulk} < 0.025$) provoke a typical cycle on the methane conversion as a function of sequential changes in temperature. The effect of sequential changes in reaction temperature on the conversion of methane and selectivity to syngas in the POM reaction has been previously observed when using Rh- and Ni-supported catalysts [5,10]. For nickel catalysts, when the temperature is below 800°C approximately, both conversion and selectivity do not increase appreciably with stepwise increasing reaction temperature. A further increase in reaction temperature results in an abrupt increase in conversion. This phenomenon is related to alterations in the oxidation state of the metallic active phase. In the first step, H_2 is generated by methane cracking reaction (at temperatures around 800°C) and then this H_2 provokes NiO reduction to metallic Ni, which is the actual active phase. The presence of O_2 seems to be responsible for the strong inhibition in the reduction of NiO and in this way it prevents the lower ignition temperature. Fig. 2 presents the cycle for the case of POM reaction; as it can be observed, the ignition temperature is approximately 70°C higher for Ni than for SnNi 003. The lower ignition temperature for SnNi 003 follows the same tendency observed in the reduction peak temperatures determined by TPR (Fig. 1). The same behavior was obtained for MR reaction.

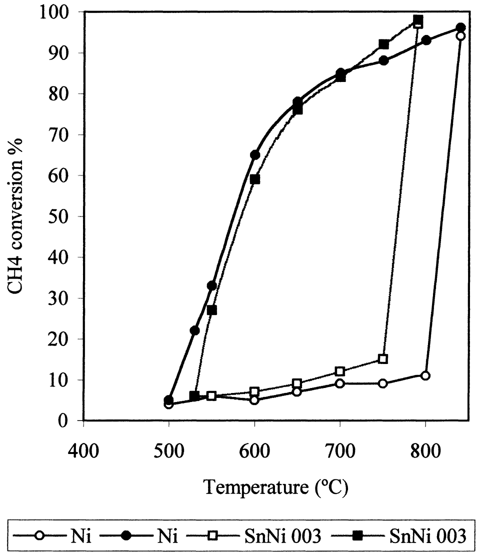

Fig. 2. Effect of reaction temperature on CH_4 conversion for Ni and SnNi 003 fresh catalysts. POM reaction ($N_2/CH_4/O_2 = 11/2/1$). Empty symbols: stepwise increase of temperature; full symbols: stepwise decrease of temperature.

Cycles shown in Fig. 3 for R reaction show an ignition temperature around 700°C for Ni and SnNi 003 catalysts; this temperature is fairly below the temperatures corresponding to MR and POM reactions. These results show that oxygen competes with methane in a stronger way than carbon dioxide in the cracking reaction and in hydrogen generation.

The fact that the Ni catalyst and the SnNi 003 bimetallic catalyst present the same behavior with respect to sequential changes in temperature (Figs. 2 and 3) and similar reactivity (Table 3) would indicate that the reaction mechanism and the number of active sites for these reactions are not appreciably modified for these Sn concentrations ($Sn/Ni^{bulk} < 0.025$).

In Fig. 4, thermogravimetric diagrams are presented, corresponding to the treatment of fresh catalysts in oxidized state, for heating and cooling processes when the feeding mixture corresponds to that of the POM reaction. During the heating process, for Ni and SnNi 003 catalysts, an abrupt weight change occurs and it is considered that this is the activation temperature of methane. At this temperature, a weight decrease is

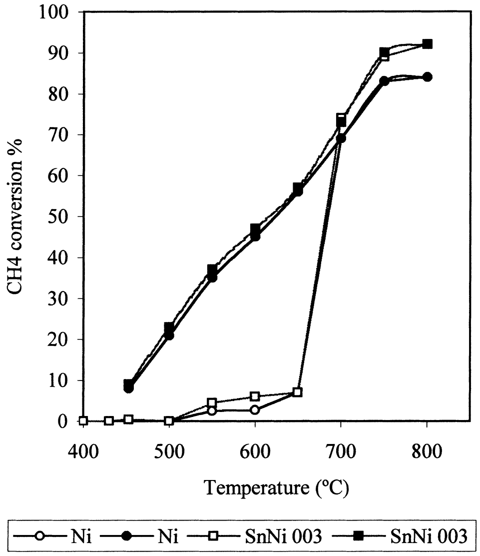

Fig. 3. Effect of reaction temperature on CH_4 conversion for Ni and SnNi 003 fresh catalysts. R reaction ($N_2/CH_4/CO_2 = 6/1/1$). Empty symbols: stepwise increase of temperature; full symbols: stepwise decrease of temperature.

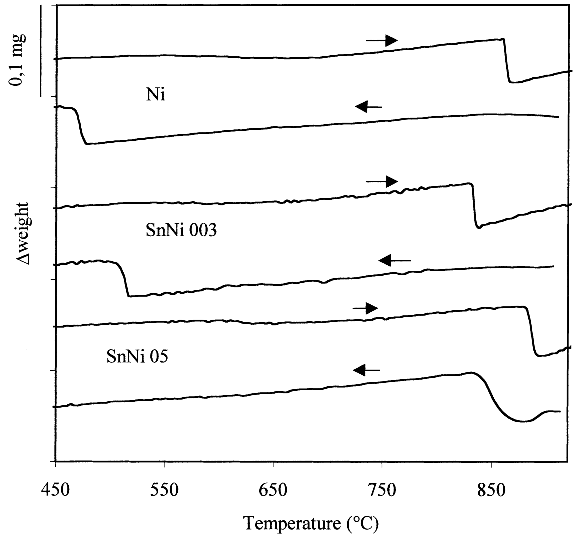

Fig. 4. Variation of sample weight (mg) as a function of temperature (°C) for Ni, SnNi 003 and SnNi 05 fresh samples. Feed composition $He/CH_4/CO_2 = 11/2/1$ (each scale unit = 0.1 mg). (→) heating process; (←) cooling process.

observed as a result of the metallic oxide reduction and, immediately after that, a weight increase starts due to methane cracking with carbon deposition. It can be seen that the activation temperatures are quite similar to the ones obtained in the cycles of Fig. 2. During the cooling process, again for Ni and SnNi 003 samples, a weight increase is detected as a consequence of the re-oxidation of the active phase. The re-oxidation occurs at temperatures near 500°C, which corresponds to the end of reactions whose cycles are shown in Fig. 2.

For SnNi 05 catalyst, on the other hand, the weight change is only observed at temperatures around 900°C, which is probably due to the methane thermal activation and not a consequence of a catalytic effect. During the cooling process, the re-oxidation of the bimetallic phase occurs at temperatures around 800°C. The reduction and the oxidation are produced in a small temperature interval, always over 800°C. This explains the almost null activity levels of the catalytic systems more tin concentrated under the operating conditions interesting for this study.

As it was previously mentioned in Section 1, the deactivation, both by sintering and by carbon formation is thermodynamically and kinetically promoted, under the operating conditions corresponding to POM, R and MR reactions, and therefore, the analysis of the stability of the active phase is a very important fact.

Figs. 5a–c show the evolution of the activity coefficient a_{CH_4} as a function of time for POM, MR and R reactions for Ni and SnNi samples. A very important aspect that arises from these figures is that the presence of O_2 as reactive plays a fundamental role; as the O_2 concentration decreases, the stability also decreases according to the sequence POM > MR $\gg$ R. In all cases, but especially for R reaction, the bimetallic catalyst improves markedly its stability. It is observed in Table 4 that the a_{CH_4}

Table 4
Stability results: a_{CH_4} (measured after 24 h on stream at 700°C) and wt.% C (measured by TPO/TGA) (for experimental conditions, see the text)

Reaction	Ni		SnNi 003	
	a_{CH_4}	wt.% C	a_{CH_4}	wt.% C
POM	0.95	0.03	0.96	0.03
R	0.52	3.75	0.87	0.12
MR	0.91	0.15	0.93	0.05

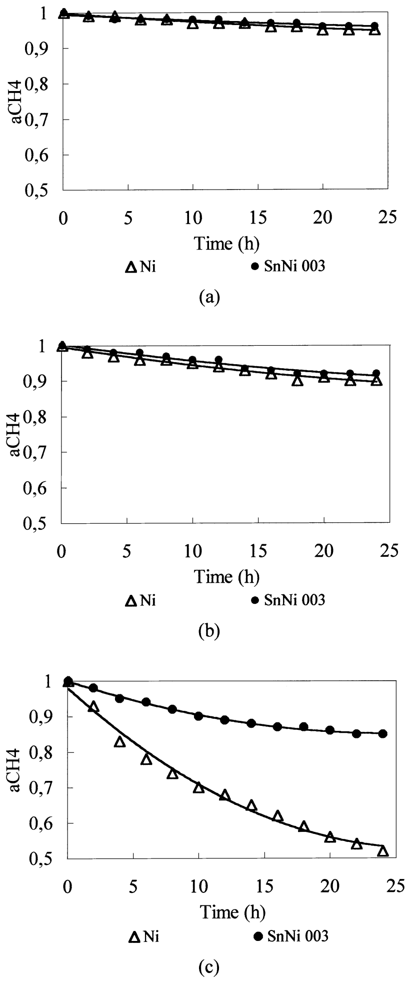

Fig. 5. Stability of Ni and SnNi 003 catalysts submitted to POM reaction (a), MR reaction (b) and R reaction (c).

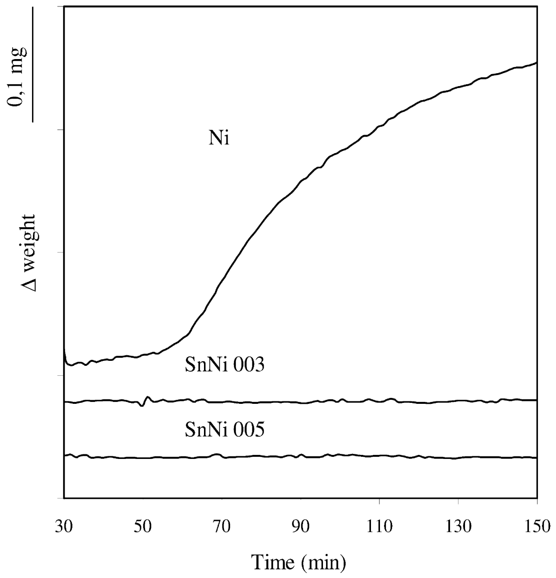

Fig. 6. Rate of carbon formation for Ni, SnNi 003 and SnNi 005 catalysts. Feed composition: $He/CH_4/CO_2 = 6/1/1$, temperature 700°C (each scale unit = 0.1 mg).

coefficient measured at $t = 24$ h passes from 0.52 to 0.87, when the Ni catalyst is promoted by Sn. Table 4 pointed out the percentages of carbon values determined by TPO/TGA for post-reaction samples; the carbon content follows the order POM $<$ MR $\ll$ R according to the stability sequence previously mentioned; therefore, the deactivation observed may be surely assigned to carbon formation.

Taking into account these results, another series of thermogravimetric experiments were designed using the feed corresponding to R reaction at 700°C in order to analyze the rate of carbon formation (Fig. 6). Then, the coked samples coming from the previous assay were cooled up to room temperature in He flow and submitted to a TPO/TGA test whose diagrams are shown in Fig. 7. Results from Figs. 6 and 7 show that the carbon formation is strongly inhibited in the presence of very low Sn concentrations. The diagrams in Fig. 7 represent the derivatives of weight changes (by oxidation and gasification of carbon) as a function of temperature, noticing that the carbon is eliminated in an oxidizing mixture between 550 and 600°C.

The catalytic results presented here, activity and stability, show important aspects in the behavior of tin modified catalysts. For the lower tin concentrations studied ($Sn/Ni^{bulk} < 0.025$), the carbon formation is almost completely inhibited, as it is observed in thermogravimetric diagrams (Figs. 6 and 7) and in the stability curves (Fig. 5). On the other hand, the rate of production of synthesis gas suffers only a little variation for these compositions ($0 < Sn/Ni^{bulk} < 0.025$).

The performance observed offers an interesting perspective for the use of these nickel-based catalysts modified by tin in the obtention of syngas from natural gas, especially via CO_2 reforming. The results presented here can be interpreted in the light of the reaction mechanisms suggested in the literature for the R reactions.

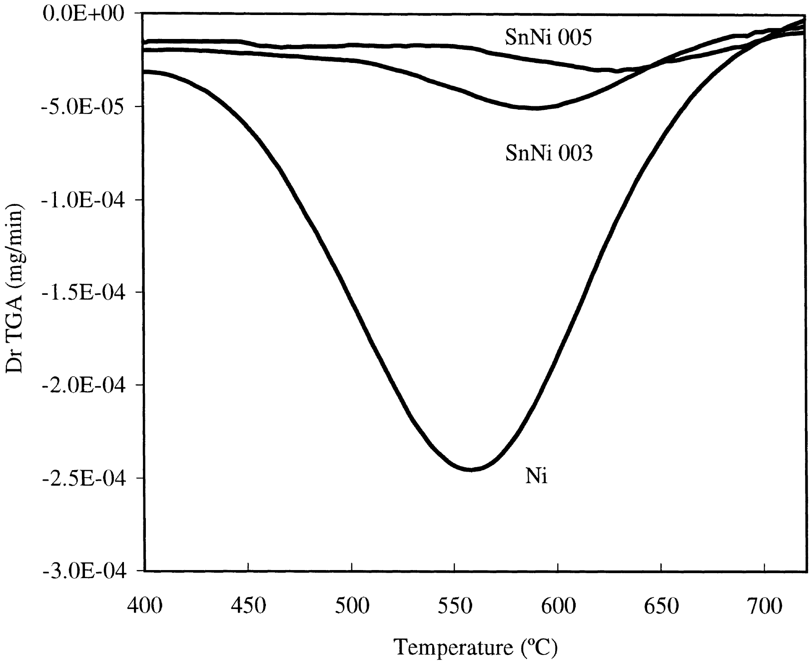

Fig. 7. Derivative of weight variation ($\mathrm{mg\,min^{-1}}$) as a function of temperature (°C) for Ni, SnNi 003 and SnNi 005 coked samples.

In relation to the mechanism of POM reaction, there have been proposed a one-step (or direct transformation) and a two-step mechanisms, in which the total combustion of a part of the CH_4 occurs in the first step, and the rest of the CH_4 reacts with the combustion products in the second step. In our case, a scheme based exclusively on a two-step mechanism would not be useful to explain the lower activity determined for R and MR reactions with respect to POM reaction. For R and MR reactions, the addition of CO_2 should produce an increment in the activity of MR reaction, but this phenomenon is not observed in our experiments. On the other hand, experiments carried out for POM reaction as a function of residence time show that CO and CO_2 are primary reaction products. Therefore, it is reasonable to suggest that our results are compatible with the coexistence of two simultaneous, one- and two-step, mechanisms.

Some authors have proposed superficial carbon species totally dehydrogenated, as intermediates in the conversion of methane to syngas [15,16,34,35]. This would mean that synthesis gas and carbon formation reactions would pass through the same intermediates coming from the cracking stage of methane. However, this explanation seems to be contradictory with the differences observed in relation to the influence of tin ($0 < \mathrm{Sn/Ni^{bulk}} < 0.025$) on the methane to syngas and carbon formation reaction rates. Some other authors state that the mechanism of syngas reaction from methane requires the formation of partially dehydrogenated species ($CH_x, x > 0$) [14,17]. Our results can be analyzed on the basis of this kind of mechanisms. Following is the reaction scheme presented by Qin et al. [14]:

$$\left.\begin{array}{ll}
\text{(a)} & CH_4 + 2S \rightarrow CH_3\text{–}S + H\text{–}S \\
\text{(b)} & CH_3\text{–}S + S \rightarrow CH_2\text{–}S + H\text{–}S \\
\text{(c)} & CH_2\text{–}S + S \rightarrow CH\text{–}S + H\text{–}S \\
\text{(d)} & CH\text{–}S + S \rightarrow C\text{–}S + H\text{–}S
\end{array}\right\} \text{CH}_4\text{ activation}$$

$$\left.\begin{array}{ll}
\text{(e)} & CO_2\text{–}S + 2S \rightarrow CO\text{–}S + O\text{–}S \\
\text{(f)} & O_2 + 2S \rightarrow 2O\text{–}S
\end{array}\right\} \text{O–S formation}$$

$$\left.\begin{array}{ll}
\text{(g)} & CH_x\text{–}S + O\text{–}S \\
 & \quad +(x-1)S \\
 & \qquad \rightarrow CO\text{–}S + xH\text{–}S \\
\text{(h)} & CO\text{–}S \rightarrow CO + S \\
\text{(i)} & 2H\text{–}S \rightarrow H_2 + 2S
\end{array}\right\} \text{CO and H}_2\text{ formation}$$

The scheme of reactions (a)–(i) allows to explain the differences of behavior between POM, MR and R processes. Assuming as acceptable that the global activity is determined by the rate of CH_4 activation and by the reaction between CH_x–S and O–S species, the difference in reaction rates between POM and R processes is the route for supplying O–S ((f) versus (e)). The lesser contribution of O–S would be responsible for the lower reaction rate of R process, which allows the development of intermediate species that lead to the formation of carbon deposits in greater proportion. Under the operating conditions employed for the R reactions ($T > 500^\circ C$), part of the adsorbed O atoms (O–S, stage (f)) can be desorbed and transformed in atomic oxygen in the gas phase ($O\text{–}S \rightarrow O_{gas} + S$). These O atoms are highly reactive and are able to produce the methane oxidation to CO_2 and H_2O. Therefore, the coexistence of both reaction mechanisms (one- and two-step) for POM reaction may be explained with the scheme proposed by Qin et al.

The stages (a)–(d) correspond to the activation of methane to carbon through successive C–H cracking steps. These steps must take place on sites formed by ensembles of several metallic atoms. If the C–S species are of the type C–Ni_3, as proposed by Demicheli et al. [21], seven Ni atoms are required per active site for carbon formation. Taking into account that SnNi 003, SnNi 005 and SnNi 01 catalysts correspond to superficial atomic ratios Sn/Ni of 6, 10 and 20% (see Table 1), respectively, it is acceptable to suppose that small amounts of tin deposited selectively on Ni are enough to destroy many active sites for carbon formation. On the contrary, the formation of synthesis gas passes through stage (g), where CH_x–S reacts with O–S species to give CO–S and H–S, which are finally desorbed to the gaseous phase as syngas ($CO + H_2$). Since CH_x–S corresponds to a partially dehydrogenated species ($x = 1$, 2 or 3), the activation stage of methane also requires ensembles of several nickel atoms, but these ensembles are not necessarily of the same size as the ones needed for carbon formation. This may explain why only concentrations of tin over $Sn/Ni^{bulk} > 0.025$ (which implies a superficial atomic concentration of 50% approximately in Sn, Table 2), inhibit the formation of synthesis gas. Some recent papers suggest that for R reaction performed on Ni/Al_2O_3 catalysts, the number of hydrogen atoms contained in the superficial species CH_x–S is between 2 and 3 [36,37]. If this is the case, syngas formation would proceed on active sites composed of ensembles of 3 or 4 Ni atoms, and so, the promoting effect of tin atoms in intimate contact with nickel would be similar to what is proposed by Rostrup-Nielsen [17,38] for the case of partly sulfur-poisoned nickel catalysts.

Taking into account these interpretations, it may be concluded that carbon formation reaction is more structure-sensitive than syngas formation reactions. The high sensitivity of the synthesis gas and carbon formation reactions to the Sn/Ni ratio evidences the importance of using a controlled methodology for the addition of promoter to assure the achievement of very well-defined supported active phases. The SOMC/M technique used in this work allows to obtain bimetallic catalysts with very low Sn/Ni atomic ratios, having excellent stability with respect to the carbon deposit without affecting the reactions of synthesis gas formation for the three studied processes (POM, R and MR).

4. Conclusions

- SnNi catalysts supported on a modified α-Al_2O_3 were prepared using a controlled technique (SOMC/M). This methodology allows to obtain very well-defined active phases, with low Sn/Ni^{bulk} values and a specific interaction between both metals.
- SnNi catalysts had a very high resistance to carbon deposition for POM, MR and R reactions. For tin concentrations below $Sn/Ni^{surf} < 0.5$ ($Sn/Ni^{bulk} < 0.025$), SnNi phases show very good levels of activity and selectivity to syngas, similar to the monometallic Ni catalysts.
- Catalytic activity for SnNi catalysts ($0 < Sn/Ni^{bulk} < 0.025$) follows the sequence POM > R ≅ MR. These results would be compatible with the coexistence of two simultaneous mechanisms (one-step and two-step) for POM reaction.
- The differences in the behavior of syngas and carbon formation reactions in relation to Sn/Ni ratio may be explained considering that carbon formation reaction is more structure-sensitive than syngas formation reactions, which emphasizes the importance of using a controlled methodology for

the addition of tin, to assure the achievement of very well-defined active phases.
- For Sn/Ni^{bulk} atomic ratios under 0.025, ensembles of Ni are still available for the dissociation of CH_4 into CH_x ($x = 2, 3$) intermediate species for syngas formation, but not for the formation of C species, which could dissolve in Ni crystals, giving rise to the nucleation of whisker carbon.
- R reaction shows the highest tendency to deactivation due to carbon deposition. The presence of O_2 strongly diminishes this tendency; therefore, it is worth considering the addition of O_2 in the feeding mixture of CO_2 reforming, as a way of improving the stability of Ni-based catalysts.

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