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New catalysts with low amounts of active phase for CPO processes

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Abstract

The preparation and characterization of different catalysts containing equal amounts of Ni (0.660 wt.%) and Rh (0.022 wt.%) and their catalytic performances and stability in CPO of methane in hard reaction conditions have been investigated. All the catalysts were obtained from hydrotalcite-type precursors (HT), prepared according to different methodologies: (a) impregnation of the active phase on a support derived from a HT precursor, (b) coprecipitation, inserting Ni and Rh inside the HT precursor, or (c) coprecipitation on a support (α-Al_2O_3) of a HT precursor containing the active metals. The different present phases as a function of the preparation method have been identified. The observed scale of activity in CPO of methane may be attributed to the dispersion of the metal particles and to the different surface area values of the catalysts.

Keywords: Catalytic partial oxidation of methane; Hydrotalcite-type catalysts; Impregnation; Bulk catalysts; Supported catalysts

1. Introduction

The use of natural gas as a raw material is a future goal of strategic relevance, because of the impending decline and cost of fossil-oil resources and, contemporarily, thanks to the large amounts of natural gas available worldwide. The economy of its utilization is related to the activation of methane [1–3]. The transformation of natural gas in synthesis gas ($CO + H_2$) by catalytic partial oxidation (CPO) is a subject of relevant industrial interest [4] especially for the conversion of methane into hydrogen in small-scale units. A great deal of efforts has been focused by academic and industrial research on the partial oxidation of methane that might represent an alternative to the steam reforming of methane, which is energy intensive and requires high investment costs. Compared to steam reforming, it is attractive because of its mild exothermic heat of reaction and the suitable H_2/CO ratio for downstream processes, such as methanol and Fischer–Tropsch syntheses. The production of hydrogen by coupling partial oxidation and water gas shift reaction is also interesting, if small-sized facilities do not justify expensive steam reforming furnaces.

Using CPO process, high methane conversion and synthesis gas selectivity can be obtained at low residence time [5] due to the high temperature reached in the reaction. Nevertheless, the temperature control and the catalyst activity and stability require further improvement to avoid homogeneous reactions at high pressure to avoid sintering of the active phase.

The catalysts reported to be active in the CPO process are either noble metals [1,6–8] or Ni-based systems [9–14]. An innovative strategy able to improve the catalyst stability is the use of noble metal and Ni-based catalysts derived by the reduction of crystalline oxide precursors [15,16].

Aim of this contribution was to prepare and characterize catalysts containing low amounts of active metals (Rh and Ni) using different preparation techniques in order to improve the catalytic performances and stability in hard reaction conditions (i.e. high temperatures and GHSV values). The catalytic behavior is a key point for the process application, since the catalyst activity and selectivity strongly affect the reaction, avoiding any increase in temperature, which favors the contribution of homogeneous reactions. On the other hand, high temperatures and space velocities require a high thermal

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and mechanical stability of the catalyst, to avoid any loss of activity.

The preparation and the study of new catalysts based on hydrotalcite type (HT) anionic clays containing transition metals faced these problems, allowing to control the catalytic properties of the metal clusters by changing the composition of the HT precursor in which the metal is inserted.

2. Experimental

The study was focused on the comparison of different catalysts containing low amounts of active phase, i.e. Ni (0.660 wt.%) and Rh (0.022 wt.%) (Table 1 and Fig. 1).

In the first catalyst (CAT1), the active elements were introduced by impregnation, using a support obtained from a HT precursor containing silicates (Ex-HT silicate Mg_{80}/Al_{20}). The second catalyst (CAT2) was prepared as an example of bulk catalyst, inserting the active elements in the HT precursor by coprecipitation. The last sample (CAT3) was prepared by supporting an HT phase containing the active metals on α-Al_2O_3, preliminary washcoated by Disperal® (Condea).

The hydrotalcite type precursors were prepared by coprecipitation at constant pH by dropping a 0.2 M aqueous solution containing the nitrate salts of the metal ions into a solution containing the silicates (sodium silicate solution, NaOH ($\geq$10%), SiO_2 ($\geq$27%), Aldrich). The pH was kept constant by NaOH addition (10.5 ± 0.2). The addition of the cation solution was carried out over 20 min; the obtained precipitate was kept in suspension under stirring at 60 °C for 45 min, then filtered and washed with distilled water until a Na_2O content lower than 0.02 wt.% was obtained. The precipitate was dried overnight at 100 °C.

2.1. Preparation of CAT1

The support hydrotalcite precursor was prepared as describe above using a cation solution containing $Mg(NO_3)_2 \cdot 6H_2O$ (99%) and $Al(NO_3)_3 \cdot 9H_2O$ (98%). After washing and drying, the precursor was calcined at 900 °C to obtain the support. The active metals were introduced on the powder of the support by incipient wetness impregnation using an aqueous nitrate solution ($Ni(NO_3)_2 \cdot 6H_2O$ (99%) and Rh(III) nitrate solution). The impregnated sample was dried at 120 °C for 2 h and then calcined at 900 °C for 12 h.

2.2. Preparation of CAT2

The hydrotalcite type precursor was prepared using a cations solution containing: $Ni(NO_3)_2 \cdot 6H_2O$ (99%), Rh(III) nitrate solution, $Mg(NO_3)_2 \cdot 6H_2O$ (99%) and $Al(NO_3)_3 \cdot 9H_2O$ (98%) in the right molar ratio. After washing and drying the precursor was calcined at 900 °C for 12 h.

2.3. Preparation of CAT3

The support of the third sample (α-Al_2O_3, Alcan chemicals Europe, 4 m^2/g), was washcoated using a primer, to create on the α-Al_2O_3 some OH groups to which the hydrotalcite type precursor can be attached. The bohemite primer was prepared by dispersing the Disperal® (Condea) in HNO_3 aqueous solution. After mixing for 10 min, a stable dispersion of bohemite was obtained. The support, α-Al_2O_3, in the right molar ratio, was added very slowly to the bohemite dispersion and then kept under stirring for at least 30 min at room temperature. The slurry was dried at room temperature overnight. Then the obtained α-Al_2O_3/Disperal® was added to the aqueous solution of the silicates and kept under stirring at 50–60 °C, forming a homogeneous dispersion. The 0.2 M aqueous solution of the nitrates of the metals was prepared and dropped into the silicates/α-Al_2O_3/Disperal® dispersion, maintaining the pH constant (10.5 ± 0.2). At the end of the dropping, the solution was left under stirring for 45 min and then filtered. After washing and drying the catalyst was dried at 100 °C overnight and then calcined at 900 °C for 12 h.

2.4. Catalytic tests

Before the CPO tests the catalysts were reduced at 750 °C in an equimolar H_2/N_2 flow of 7 l/h. The catalytic tests for the CPO reaction were carried out in a quartz reactor (i.d. 8 mm) filled with 0.5 g of catalyst with particle size between 0.841 and 0.400 mm in order to avoid pressure drop, giving a bed length of about 2 cm. The reactor is inserted in an electric oven, where three gas mixtures have been fed: (1) $CH_4/O_2/He = 2/1/20$ (v/v), $T_{oven} = 500$ °C, $\tau = 65$ ms; (2) $CH_4/O_2/He = 2/1/4$ (v/v), $T_{oven} = 750$ °C, $\tau = 65$ ms; (3) $CH_4/O_2/He = 2/1/1$ (v/v), $T_{oven} = 750$ °C, $\tau = 112$ ms (being τ calculated as weight of catalyst over total flow).

The tests at 500 °C in diluted conditions are useful to discriminate among the catalysts, while the tests at 750 °C are

Table 1
Catalyst compositions, BET surface area and results of the H_2 chemisorption analyses

Sample	Description	BET surface area (m^2/g)		Metal dispersion (%)	Metallic surface area (m^2/g metal)	Crystallite size (nm)
		Precursor	900 °C			
CAT1	Impregnated sample: Rh and Ni on Ex-HT silicate $Mg_{80}Al_{20}$	138	107	1.65	10.89	61
CAT2	Bulk sample: Ex-HT silicate $Rh_{0.01}Ni_{0.57}Mg_{79.43}Al_{19.99}$	87	111	3.53	23.30	28
CAT3	Bulk sample on a support: Ex-HT silicate $Rh_{0.15}Ni_8Mg_{60}Al_{31.85}$ on α-Al_2O_3	19	25	5.11	33.64	20

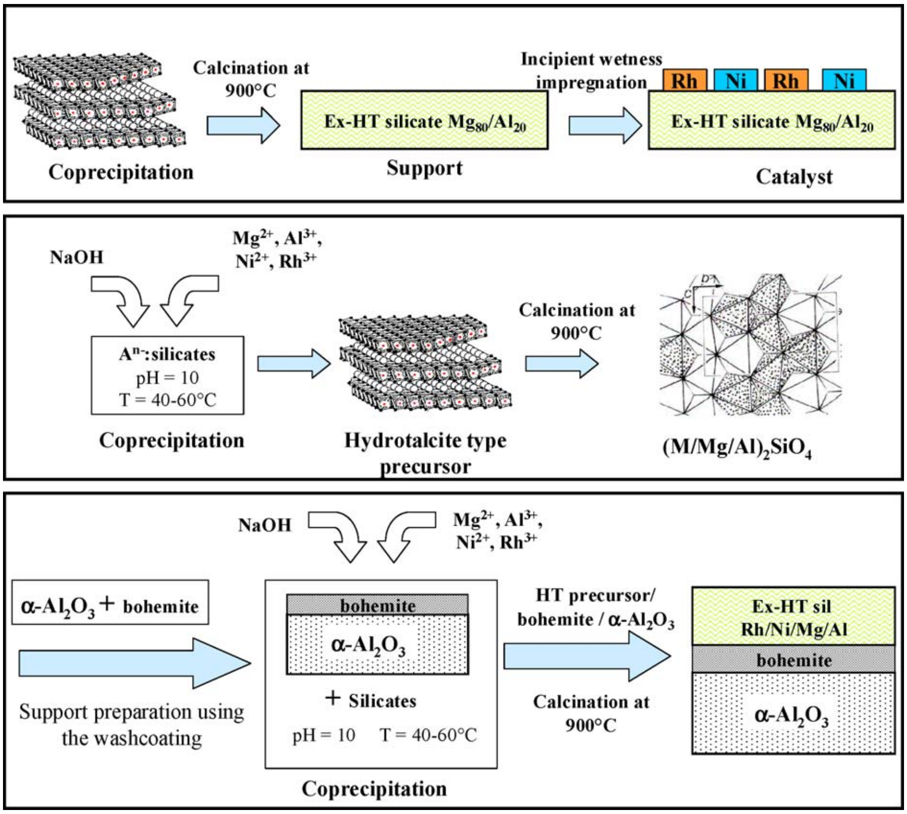

Fig. 1. Schematic preparation methods of the investigated catalysts.

closer to industrial conditions and can be useful to stress the catalyst stability.

Furthermore, all the catalysts have been subjected to deactivation tests, while keeping the catalyst in hard reaction conditions ($CH_4/O_2/He = 2/1/4$ (v/v), $T_{oven} = 750$ °C, $\tau = 65$ ms) during the day (8 h) and controlling the deactivation with tests at low temperature ($CH_4/O_2/He = 2/1/20$ (v/v), $T_{oven} = 500$ °C, $\tau = 65$ ms). The tests at low T were carried out for each 8 h run as initial tests by heating the sample from room temperature to 500 °C and feeding the dilute mixture, subsequently as final tests by cooling from the higher temperature.

The reaction products were analyzed on-line after water condensation by two gas chromatographs equipped with HWD and Carbosieve SII columns, using He as the carrier gas for the analysis of CH_4, O_2, CO and CO_2 and N_2 as the carrier gas for the H_2 analysis.

2.5. Catalysts characterization

The XRD powder analyses were carried out using a Philips PW1050/81 diffractometer equipped with a graphite monochromator in the diffracted beam and controlled by a PW1710 unit ($\lambda = 0.15418$ nm). A 2θ range from 10° to 80° was investigated at a scanning speed of 70°/h. The surface areas were determined by N_2 adsorption using a Carlo Erba Sorpty model 1700. H_2 Chemisorption analyses were performed using a Micromeritics ASAP 2020C instrument. Before analysis the samples were pre-treated evacuating up to 10 μmHg, then the samples were reduced under H_2 flow for 2 h at 750 °C (to simulate the real pre-reduction conditions) afterwards a further evacuation was carried out in order to remove all H_2. The H_2 chemisorption analysis was carried out at 35 °C.

3. Results and discussion

The impregnated (CAT1) and the bulk (CAT2) catalysts present high surface area values, typical of the HT samples. CAT3 – in which the HT active phase is supported on α-Al_2O_3- shows a surface area only slightly higher than that of the precursor, due to the presence of the bulk phase precipitated on the support (Table 1). In fact the surface area of the α-Al_2O_3 is 4 m^2/g, while that of the precursor of the support α-Al_2O_3/Disperal® is 19 m^2/g. Furthermore the final catalyst (after calcination at 900 °C, in which the bohemite has been changed to α-Al_2O_3) still shows a surface area value of 25 m^2/g, due to the high surface area of the bulk phase obtained from hydrotalcite type precursor (in this case 1/12 (wt/wt) of the whole sample). This means that the catalyst surface is probably similar to that of the bulk catalyst (CAT2).

The XRD pattern of the Ex-HT sil Mg_{80}/Al_{20}, calcined at 900 °C, used as support, and those of the catalyst impregnated with Rh and Ni (CAT1) are reported in Fig. 2. The impregnation gives rise to a decrease of crystallinity of Mg_2SiO_4 and of MgO. After calcination the XRD pattern is similar to that of the support. The XRD pattern of the spent catalyst is also reported and shows no differences if compared to that of the fresh

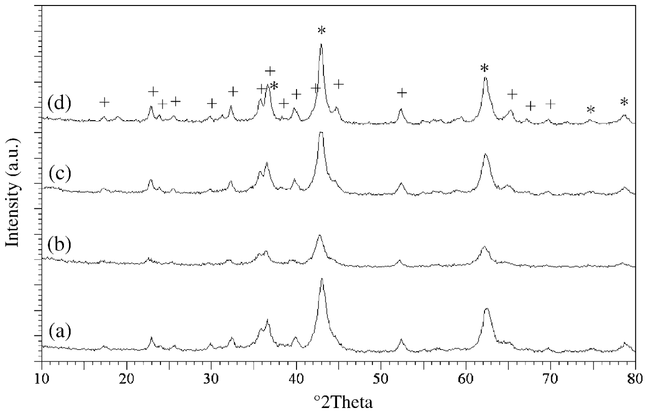

Fig. 2. XRD patterns of CAT1 in different steps of preparation and after reaction: (a) Ex-HT $Mg_{80}Al_{20}$, support calcined at 900 °C, (b) Ex-HT $Mg_{80}Al_{20}$ impregnated with Rh and Ni, not calcined, (c) Ex-HT $Mg_{80}Al_{20}$ impregnated with Rh and Ni, calcined at 900 °C and (d) Ex-HT $Mg_{80}Al_{20}$ impregnated with Rh and Ni, calcined at 900 °C, used sample (+) Mg_2SiO_4 and (*) MgO.

catalyst. The very low amounts of Rh (0.022 wt.%) and Ni (0.66 wt.%) are not detectable.

CAT2, containing the same amount of Ni and Rh of the previous catalyst, has been prepared as a bulk Ex-hydrotalcite catalyst. The XRD patterns of the fresh and used samples reveal the presence of Mg_2SiO_4 and of MgO phases (Fig. 3). There are no phases containing only Rh or Ni in both samples, because of their low amounts.

The XRD patterns of the sample Ex-HT silicate $Rh_{0.15}Ni_8Mg_{60}Al_{31.85}$/Disperal/α-$Al_2O_3$ (1/1/10, wt), CAT3, in different steps of preparation are reported in Fig. 4. In the final catalyst, besides the support phase, the reflections of Mg_2SiO_4 are present together with a $MgAl_2O_4$ defective phase, even if the intensities of the peaks are low, according to the small amount of HT-silicate present in this catalyst (1/12 of the sample).

The H_2 chemisorption analyses show that CAT1 (impregnated sample) presents the lowest metal dispersion and the highest apparent crystallite size of the metals, probably due to weak interaction of the metal with the support that causes an easier sintering of the metals.

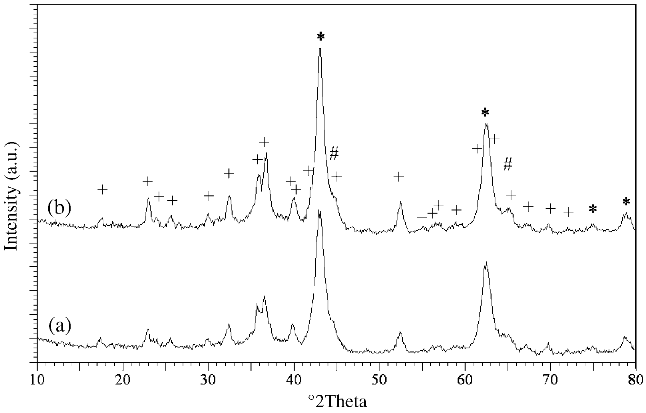

Fig. 3. XRD patterns of CAT2, Ex-HT silicate $Rh_{0.01}Ni_{0.57}Mg_{79.43}Al_{19.99}$ (a) before and (b) after reaction. (+) Mg_2SiO_4, (*) MgO and (#) $MgAl_2O_4$ defective phase.

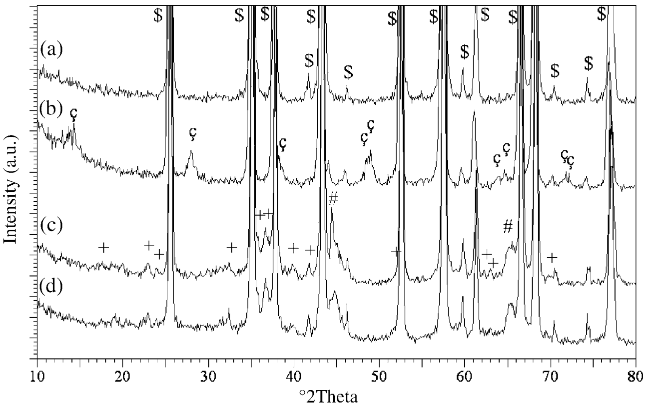

Fig. 4. XRD patterns of CAT3 in different steps of preparation and after reaction (a) α-Al_2O_3, (b) Disperal/α-Al_2O_3, (c) Ex-HT silicate $Rh_{0.15}Ni_8Mg_{60}Al_{31.85}$/Disperal®/α-$Al_2O_3$ and (d) used Ex-HT silicate $Rh_{0.15}Ni_8Mg_{60}Al_{31.85}$/Disperal®/α-$Al_2O_3$. ($) α-Al_2O_3, (ç) bohemite, (+) Mg_2SiO_4 and (#) $MgAl_2O_4$ defective phase.

CAT2 and CAT3, in which the metals are inserted inside the HT precursors, the metal dispersions are higher than that of the impregnated one. The stronger interaction of the Ni and Rh with the support leads to smaller and stable particles, even if Ni and Rh inserted in the bulk of the catalysts are expected to be more difficult to reduce. The difference between the two coprecipitated samples is that in the case of CAT2 the concentration of the metals, in the bulk Ex-HT phase, is lower because the whole catalyst is the mass of the bulk, while for CAT3 the mass of the bulk containing the metals is 1/12 of the whole catalyst and it is concentrated on the catalyst surface. Probably not all the active metals are reduced in CAT2 and CAT3, however, the stronger interaction of Ni and Rh with the support phase is responsible of a lower sintering in such a hard reduction step. Moreover, the dispersion of the metals in CAT3 is higher than the other coprecipitated catalyst due to the higher concentration of the active metals on the surface.

In the catalytic tests at low temperature, CAT1 showed very low activity while at high temperature the activity was good (Fig. 5). The possibility of a lack of activation of the active phase by the reductant mixture H_2/N_2 does not seem possible, since the metals have been impregnated on the support surface. Therefore, it may be hypothesized that in the initial conditions (2/1/20 (v/v), 500 °C) the active metals are re-oxidized by the reaction mixture. The interaction of the impregnated metals and the support is weak and they are easily re-oxidized.

Also in the lifetime test, at low temperature (500 °C) the catalytic activity was very low, thus confirming that for this catalyst, these conditions produce an oxidative ambient. When feeding the $CH_4/O_2/He = 2/1/4$ mixture at 750 °C a small increase in the yield of syn gas was observed between the first day (8 h) and the second day on stream. Then the activity remained constant (Fig. 6).

The bulk catalyst (CAT2) presented very low activity in the initial test. With increasing the oven temperature to 750 °C, the CH_4 conversion increased remarkably. By feeding the concentrated mixtures, the methane conversion was almost constant reaching values around 86%.

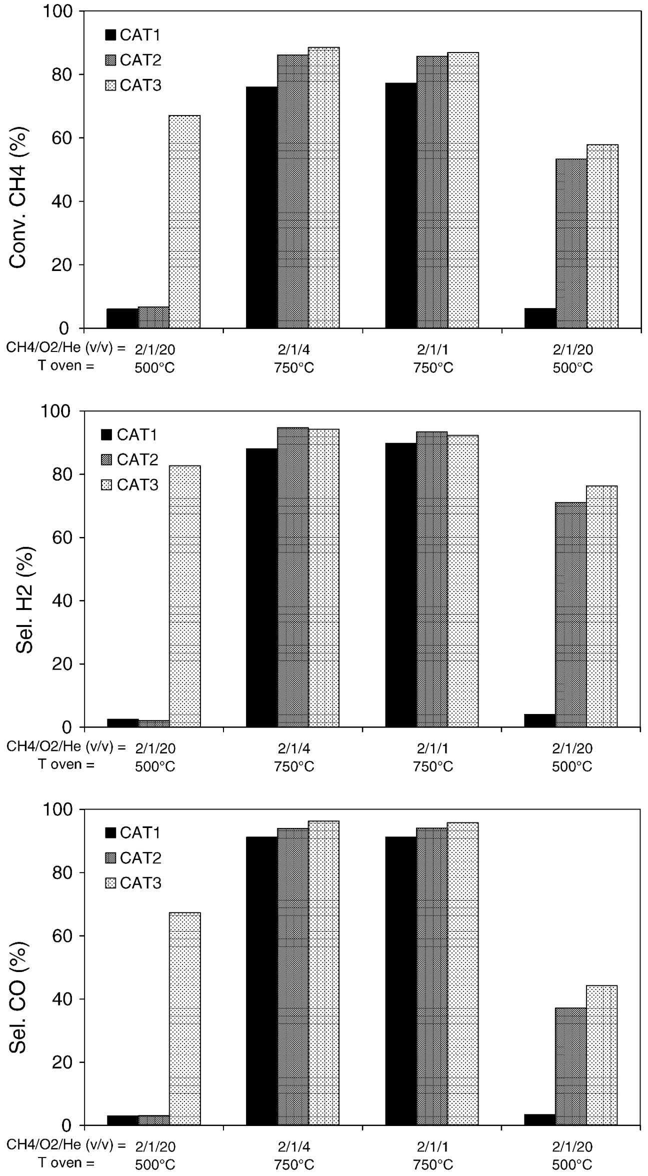

Fig. 5. Comparison of CH_4 conversions, H_2 and CO selectivities of the investigated catalysts in different reaction conditions.

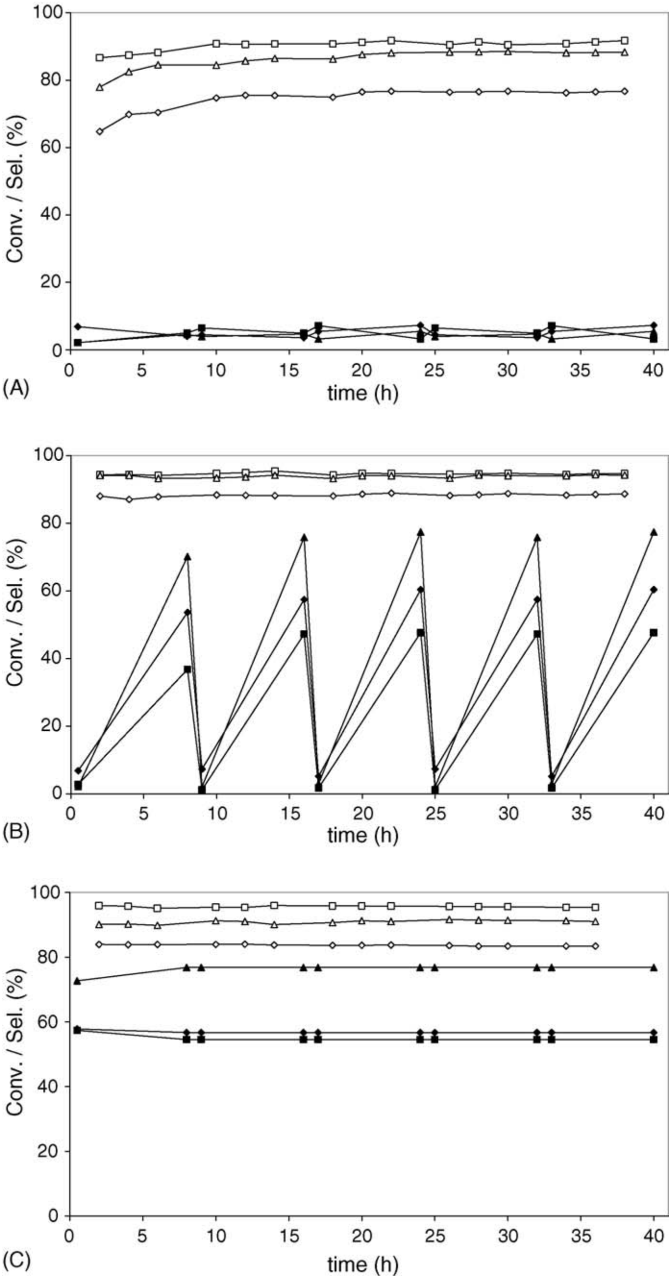

Fig. 6. Results of the tests carried out as a function of time-on-stream on (A) CAT1, (B) CAT2, (C) CAT3. (◆) Conversion CH_4, (■) selectivity CO and (▲) selectivity H_2; reaction conditions: $T_{oven} = 500$ °C, $CH_4/O_2/He = 2/1/20$ (v/v) and $\tau = 65$ ms. (◇) Conversion CH_4, (□) selectivity CO and (△) selectivity H_2; reaction conditions: $T_{oven} = 750$ °C, $CH_4/O_2/He = 2/1/4$ (v/v) and $\tau = 65$ ms.

In the lifetime test at low temperature the bulk catalyst presented, at the beginning of the run, very low activity, but an increase in yield of syn gas in the final tests of the day (Fig. 6). This is probably due to the effect of the initial conditions after start-up, in which the mixture was fed at 500 °C after a He stream, re-oxidizing the active phase. On the contrary, the tests at the end of the day were carried out by lowering the temperature and diluting the gas in reaction stream from hard conditions (high reducing atmosphere) while keeping the reaction running (i.e. at temperature higher than 500 °C in a H_2, CO-containing atmosphere). In fact, in these tests the bulk sample showed high activity also at low temperature. Moreover, the activity at high temperature and with 2/1/4 (v/v) mixture showed very constant results all over the 5 days (both CH_4 conversion and CO and H_2 selectivities).

The activity of CAT3 was high in all the reaction conditions both at 500 and 750 °C. The values of methane conversion and product selectivities remained almost constant also during all the deactivation test. For the diluted mixture and low temperature the catalyst showed high and constant conversion and selectivities (Fig. 6).

Therefore, the catalyst with the best performances was the supported catalyst, in particular at low temperature and with the diluted mixture, since these conditions are far from the thermodynamic equilibrium. With increasing the temperature and feed concentration, the differences between the catalysts were smoothed, although the supported catalyst showed yield in syn gas always higher than those of other catalysts. With the exception of the initial test at 500 °C with 2/1/20 (v/v) mixture, the bulk catalyst also showed interesting results.

The observed scale of activity, CAT3 (bulk on a support) > CAT2 (bulk) > CAT1 (impregnated), may be attributed to the availability and to the dimensions of the metal particles on the surface, as demonstrated by the H_2 chemisorption.

4. Conclusions

Catalysts obtained from HT precursors containing low amounts of Rh and Ni were prepared with different methodologies: (CAT1) impregnation, (CAT2) bulk coprecipitation and (CAT3) coprecipitation on α-Al_2O_3. The impregnated and the bulk coprecipitated (CAT1 and CAT2) samples present high surface area values, typical of HT samples, while the HT coprecipitated on α-Al_2O_3 presents a lower surface area value, according to that of the support. The different preparation steps of each sample were followed by XRD analysis, but for all the catalysts the active metal phases were not detectable, due to their low amounts. The H_2 chemisorption analyses show that the higher metals dispersion and the lower crystallite sizes are obtained for CAT3 and CAT2.

The samples were tested in CPO reaction, observing some interesting differences among the catalysts:

- The impregnated catalyst (CAT1) showed an easy re-oxidation of the active phase at reaction conditions far from the thermodynamic equilibrium, due to the presence of free Ni and Rh metal particles on the support surface.
- The bulk coprecipitated catalyst (CAT2) showed a difficult start-up when feeding the diluted mixture, but higher activity than that of the impregnated sample and with activation with time-on-stream attributable to the stronger interaction of the metal particles with the bulk support, that avoid easy re-oxidation.
- The HT coprecipitated on α-Al_2O_3 (CAT3) showed the best performances in all the reaction conditions probably due to the availability of the metal particles and their higher dispersion on the surface, that can affect both heat distribution and thermal profile.

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