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Role of the hydrotalcite-type precursor on the properties of CPO catalysts

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Abstract

New active and stable nano-structured catalysts obtained from hydrotalcite-type precursors (HT) have been synthesised as catalytic materials for the partial oxidation of methane. The prepared hydrotalcitic precursors containing carbonates or silicates as interlayer anions were calcined and the latter give rise to new mixed oxide and silicates phases. The calcined and reduced catalysts formed by mixed oxide and silicate phases were tested for the catalytic partial oxidation of methane (CPO). Finally, the role of the amount of the active metal and the amount of the excess of silicates inserted as anion were investigated.

Keywords: Hydrotalcite-type precursor; Nano-structured catalyst; CPO catalysts

1. Introduction

The use of natural gas as a raw material is a future goal of strategic relevance. The economy of its utilisation is related to the activation of methane [1–3]. Indeed, the direct processes to C_2-products and methanol are not attractive due to the low yields obtained. On the other hand the indirect processes to CO + H_2 (syngas) are characterised by high investment costs therefore do not allow an intensive methane exploitation. The transformation of natural gas into synthesis gas (CO + H_2) through the catalytic partial oxidation (CPO) of methane is a new route of considerable industrial interest [4] especially for the conversion of methane into hydrogen in small-scale units. The reaction has been well known since Prette et al. reported the activity of a Ni-based catalyst [5,6], nevertheless the discovery that high methane conversion and high synthesis gas selectivity can be obtained at low residence time, enhanced the interest in the partial oxidation of methane [7–9]. Many aspects of this reaction have not yet been fully clarified, but it is evident that the industrial application of the process requires improvements in the temperature control and selectivity, to avoid homogeneous reactions at high pressure [10,11], and an increase in the catalyst durability to avoid sintering of the active phase. An innovative strategy able to improve the catalyst stability is based on the use of noble metal catalysts derived by reduction of crystalline oxide precursors [12,13]. The metal support interaction in this case is expected to be stronger than that obtainable with the usual impregnation or deposition methods. This allows keeping high selectivity and temperature control with time on stream.

The aim of this contribution was the preparation and characterisation of new tailor-made materials obtained from hydrotalcite-type (HT) precursors [14,15], to be used as stable catalysts for the CPO of methane, in severe reaction conditions (i.e. high temperature and high GHSV values). The hydrotalcite-derived catalysts (ex-HT) have already been reported as effective catalysts in the production of synthesis gas, using as active phase Ni, Rh and Ni/Rh [16]. The characterisation of these catalysts has revealed that the structure is made of MgO type and spinel type phases containing Rh and/or the Ni, which can be extracted to form rather stable metal particles. A general property of the ex-HT is that the amount and the nature of M(II) and M(III) modified the ratio between MgO and spinel phases. The

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reducibility and stability of the Ni catalysts (in which Ni is preferentially present in a solid solution with Mg), are strongly affected by the Mg/Al/Ni ratio due to three main effects:

1. A low Mg content favours the formation of low active $NiAl_2O_4$.
2. Ni-rich samples exhibit low Ni^{2+} reduction temperature, and fast deactivation due to the presence of large Ni-particles [9,17].
3. A decrease in reducibility of the Ni^{2+} ions is observed for high Mg/Ni ratio, due to the low concentration of Ni in the (Ni/Mg)O solid solution.

These effects limit the activity and stability of Ni containing catalysts that require new formulation. The situation for Rh catalysts is still more complicated, since it is soluted both in the spinel type and in the MgO type phases and the Mg/Al ratio affects the distribution of Rh between the two phases. The presence of a third element can change the correlation between Mg/Al ratio, spinel/MgO phase ratio and the Rh distribution. In particular the silicate can form with Mg or Al a specific phase, which can also incorporate Rh and or Ni. Furthermore the presence of nesosilicate can improve thermal and mechanical resistance at high temperature [18]. The thermal evolution of noble metal containing catalysts with high activity prepared using hydrotalcite-type precursors with carbonate has been recently reported [19–21]. Nevertheless the comparison with the HT prepared by silicate requires further study to find a correlation between structure and reactivity in order to optimise the catalyst composition.

2. Experimental

The catalysts were obtained by calcination and reduction of hydrotalcite-type (HT) precursors with formulas reported in Table 1. They were prepared by coprecipitation at constant pH by adding a solution containing the nitrate salts of the metal ions to a solution containing a slight excess of carbonates or silicates. The pH was kept constant by NaOH additions (10.0 ± 0.2 for CO_3^{2-} and 10.6 ± 0.2). The addition of the cations solution was carried out over 20 min; the obtained precipitate was kept in suspension under stirring at 60 °C for 40 min, filtered and washed with distilled water until a Na_2O content lower than 0.02 wt.% was obtained. The precipitate was dried overnight at 90 °C, calcined at 900 °C and reduced at 750 °C in an equimolar H_2/N_2 flow of 7 l/h [18,19]. 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 catalytic tests were carried out in a quartz reactor (i.d. 8 mm) filled with 0.5 g of catalyst with particle size between 0.60 and 0.42 mm 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 feeding: (1) $CH_4/O_2/He = 2/1/20$, T(oven) = 500 °C, $\tau = 65$ ms; (2) $CH_4/O_2/He = 2/1/4$, T(oven) = 750 °C, $\tau = 65$ ms; (3) $CH_4/O_2/He = 2/1/1$, T(oven) = 750 °C, $\tau = 112$ ms (being τ calculated as weight of catalyst on total flow). The tests at 500 °C in diluted conditions are useful to discriminate among the catalysts while the tests at 750 °C are closer to industrial conditions and can be useful to stress the catalyst stability. The gas phase temperature was measured by a moveable chromel–alumel thermocouple sliding in a quartz wire inside the catalytic bed. The reaction products were analysed 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. The Oxygen conversion is complete in the whole series of the catalytic tests and the C balance is always between 98 and 102%.

3. Results and discussion

The catalysts obtained by HT precursors containing carbonates as interlayer anions have already been investigated [19,21] allowing some conclusions in terms of relative amount of MgO and spinel and in terms of Rh distribution in the oxide phases before reduction. It was found that the Rh is more soluble in the spinel-type phase than in the MgO-type phase, although the amount of MgO was higher than that of

Table 1
Composition, interlayer anion and surface area values of the samples investigated

Sample	Composition as Rh/Mg/Al (a.r.)	Anion[a]		Surface area ($m^2 g^{-1}$)		
		Type	Excess (%)	HT precursor	Calcined ex-HT	After reaction ex-HT
Rh 0.5 Carb	0.5/71/28.5	Carbonates	30	162	92	99
Rh 0.5–30 Sil	0.5/71/28.5	Silicates	30	296	108	108
Rh 0.3–30 Sil	0.3/71/28.7	Silicates	30	202	110	92
Rh 0.1–30 Sil	0.1/71/28.9	Silicates	30	186	96	92
Rh 0.1–20 Sil	0.1/71/28.9	Silicates	20	68	142	147

[a] Amount of anion used during preparation.

the spinel and increased by increasing the Mg/Al ratio. As concerns the catalytic activity, the catalysts containing the Rh only in the MgO-type phase were more active than the catalysts characterised by the presence of some Rh in the spinel-type phase. The different activity was attributed to the different crystal size of the Rh$^\circ$ deriving from the spinel that was higher than that deriving from the MgO.

In this paper, HT precursors containing carbonates or silicates as interlayer anions have been prepared. The HT precursors, either containing carbonates or silicates, show high surface areas. Both have been prepared using an excess of A^{n-} with respect to the amount required to balance the cations charge. Analysing the filtrate and the precipitate precursor containing silicates was found that almost the whole amount of silicates present in the solution has been inserted in the interlayer. This is due to the fact that the silicates have been also present in the interlayer as polisilicate anions $Si_nO_{2n+1}{}^{2-}$. Analogous results have been obtained with two other silicate catalysts prepared in the same conditions (30% excess of silicate) but changing the Rh content. The insertion of the silicates and polisilicate in the hydrotalcitic precursors affected the HT structure giving rise to a remarkable decrease in the crystallinity (Fig. 1A) with respect to the HT prepared with carbonates. The presence of silicates also affected the structure of the calcined samples, since, unlike carbonate, the silicates remained in the structure after calcinations and contributed to the final catalysts. The presence of a third component as anion in the precursor interlayer modified the structure affecting the type of phases and the Rh distribution inside them. To analyse the effect of the excess of silicate, two catalysts having the same amount of Rh have been prepared using 30% and 20% excess of silicates as compared to the charge balance of the cations.

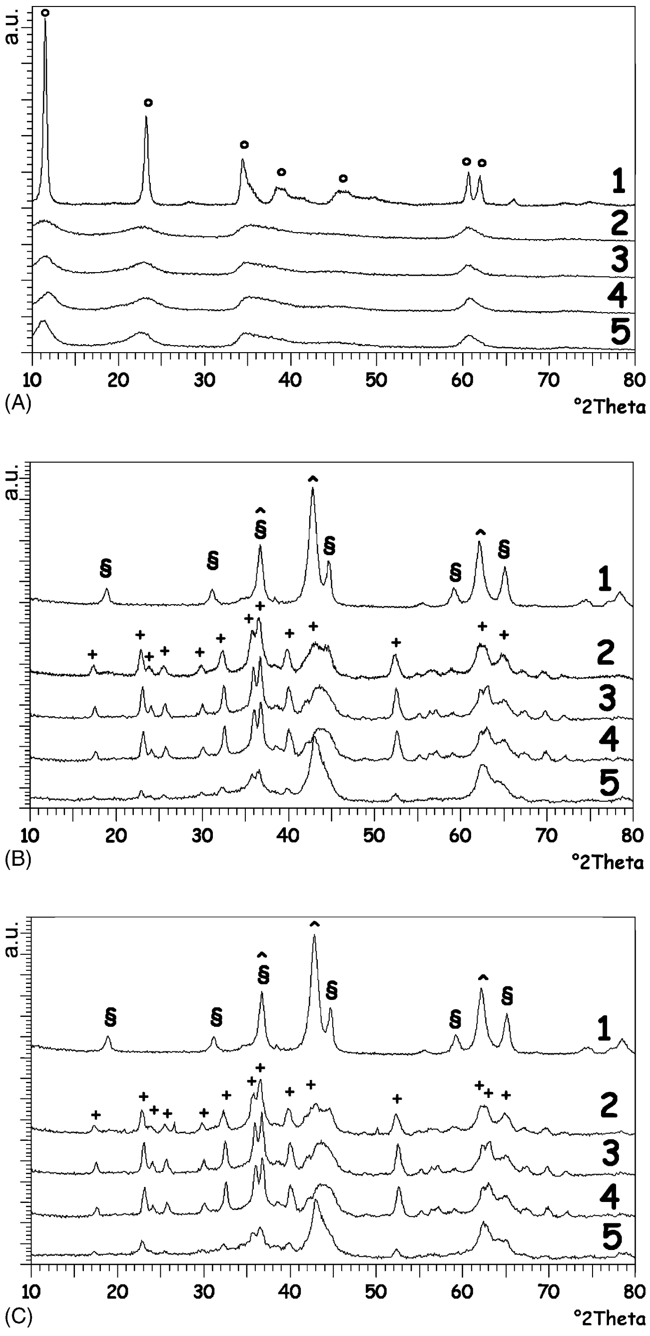

Fig. 1. (A) XRD analysis of the HT precursors of Rh/Mg/Al samples: (1) Rh 0.5 Carb; (2) Rh 0.5–30 Sil; (3) Rh 0.3–30 Sil; (4) Rh 0.1–30 Sil and (5) Rh 0.1–20 Sil (○: hydrotalcite-type phase). (B) XRD analysis of the calcined Rh/Mg/Al samples: (1) Rh 0.5 Carb; (2) Rh 0.5–30 Sil; (3) Rh 0.3–30 Sil; (4) Rh 0.1–30 Sil and (5) Rh 0.1-20 Sil ((§) spinel-type phase, (^) MgO type phase, (+) Mg_2SiO_4-type phase). (C) XRD analysis of the used Rh/Mg/Al samples: (1) Rh 0.5 Carb; (2) Rh 0.5–30 Sil; (3) Rh 0.3–30 Sil; (4) Rh 0.1–30 Sil and (5) Rh 0.1–20 Sil ((§) spinel-type phase, (^) MgO type phase, (+) Mg_2SiO_4-type phase).

The calcined sample prepared using carbonate shows a well-known XRD pattern with an MgO and a spinel phase in which Rh is soluted. The samples prepared with 30% of silicate excess all have similar XRD patterns showing the MgO phase and a forsterite-type phase Mg_2SiO_4 [22] and differs significantly from the carbonate samples due to the absence of the spinel phase. The forsterite phase is a nesosilicate, orthosilicate phase (olivine class) characterised by isolated $SiO_4{}^{4-}$ connected with Mg, Al or other cation in octahedral coordination with oxygen. The stability of this phase is given by the isolation of the $SiO_4{}^{4-}$ group that are bonded to other cations giving rise to a stable thermodynamic phase and a strong inhibiting effect to its decomposition and vaporisation [18]. The absence of other side phase containing Rh and especially Al leads to the conclusion that they are partially inserted in the new phase that will be indicated by $Mg_{2-x}M_{2/3x}SiO_4$ (M = Al, Rh). The HT Sil 30% samples also show a constant ratio between the forsterite type and the MgO type phases. On the other hand, comparing the samples containing 20% and 30% excess of silicates, the former presents a lower amount of forsterite-type phase with respect to the MgO-type phase, while the latter shows mainly the $Mg_{2-x}M_{2/3x}SiO_4$ forsterite-type structure. The surface areas decrease after calcination at 900 °C, maintaining however values of about $100\ m^2\ g^{-1}$, which are relatively high considering

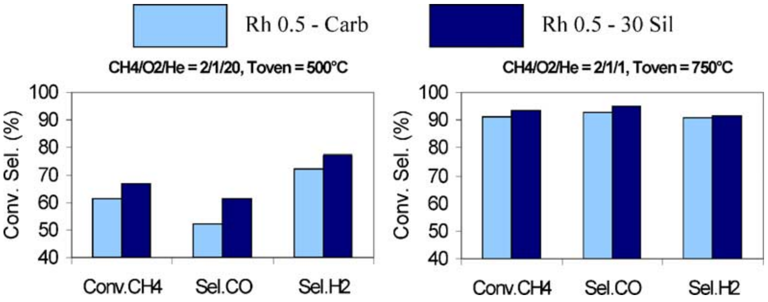

Fig. 2. Methane conversion, CO and H_2 selectivities of the ex-HT carbonate and ex-HT silicate catalysts, with atomic ratio Rh/Mg/Al 0.5/71/28.5, in two different reaction conditions: (1) $CH_4/O_2/He$ = 2/1/20, T = 500 °C, τ = 65 ms [ex-HT Sil: T_{out} = 538 °C, T_{max} = 595 °C; ex-HT Carb: T_{out} = 532 °C, T_{max} = 598 °C]; (2) $CH_4/O_2/He$ = 2/1/1, T = 750 °C, τ = 112 ms [ex-HT Sil: T_{out} = 758 °C, T_{max} = 827 °C; ex-HT Carb: T_{out} = 756 °C, T_{max} = 842 °C].

the high calcination temperature. The values were not different from the HT containing carbonate notwithstanding the different structure. Furthermore, also after the reaction the samples maintain constant surface area values, confirming the high thermal stability of this type of materials considering the drastic reaction conditions to which they were submitted.

The catalytic activity of the Rh 0.5–30 Sil was compared with the analogous catalyst obtained by HT carbonate with the same cations ratio. The results showed that the catalyst containing silicates was more active and selective towards syngas than that prepared with CO_3^{2-} (Fig. 2). This is particularly evident in the test at 500 °C that is far from the thermodynamic equilibrium (at an average gas phase temperature of 575 °C CH_4 equilibrium conversion = 70%) [9,13,19] and that shows a relatively high syngas selectivity. These results may be explained by considering the different position of the Rh in the calcined samples and its effect on the catalytic performances. In this case, the presence of silicate gives rise, after calcination, to a forsterite-type phase while the formation of the spinel phase was inhibited. The related improvement of the catalytic performances can be explained in analogy to the behaviour of the carbonate sample in which, increasing the Mg/Al ratio, the amount of the spinel type phase decreases [19–21].

The role of Rh was investigated by decreasing its amount in the catalyst prepared with 30% of silicates excess. The HT silicate catalysts containing Rh 0.3 and Rh 0.1 were tested in the laboratory plant and compared with the Rh 0.5 (Figs. 2 and 3). The methane conversion and the syngas selectivity decrease with the decrease in active metal at low temperature and in diluted conditions, confirming that these conditions can discriminate among active catalysts and are useful to verify the catalyst optimisation. At high temperature reaction conditions, the differences are less important, although present, since the CH_4 conversion and the CO and H_2 selectivities are close to the thermodynamic equilibrium values.

To study the role of the amount of silicates and, consequently, of the amount of forsterite-type phase in the final catalyst, the sample Rh 0.1–20 Sil prepared with 20% of silicate excess was compared with the analogous catalyst prepared using 30% of silicate excess with the same Rh amount.

The catalyst with the 20% of silicate excess shows higher activity and CO and H_2 selectivity with respect to the sample with the same formulation but higher amount of silicates. This is particularly clear in the tests carried out at 500 °C in diluted conditions but, although smoothed, it is also present at high temperature. Furthermore in the whole series of tests the Rh 0.1–20 Sil sample shows similar CH_4 conversion and products selectivities with respect to the Rh 0.3–30 Sil catalyst having a content of Rh three times higher (Rh 0.3 a.r.) and better results than the Rh 0.5 Carb having a Rh content five times higher (Rh 0.5 a.r.) (Fig. 4).

The high sensitivity to the type and amount of anion can be explained in terms of the effect on the matrix in which the Rh is soluted before reduction and dispersed after reduction. In particular it can be hypothesised that the maximisation of the MgO type phase and the type of side phase are the two parameters that determine the final yield in CO and H_2. In fact, in these samples, a silicate excess of 20% is enough to avoid the formation of spinel and makes predominant the MgO-type phase, which is the more active [19,21,23,24]

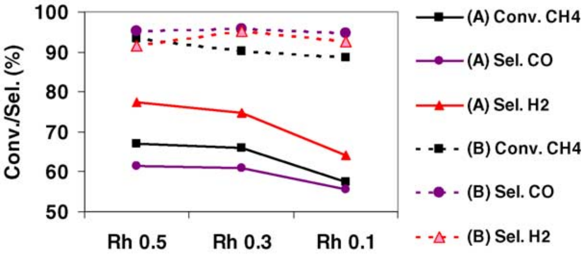

Fig. 3. Activity of the ex-HT silicate (excess 30%) catalysts containing different amounts of Rh in two different reaction conditions: (A) $CH_4/O_2/He$ = 2/1/20, T = 500 °C, τ = 65 ms (full lines) [Rh 0.5: T_{out} = 538 °C, T_{max} = 595 °C; Rh 0.3: T_{out} = 547 °C, T_{max} = 622 °C; Rh 0.1: T_{out} = 584 °C, T_{max} = 622 °C]. (B) $CH_4/O_2/He$ = 2/1/1, T = 750 °C, τ = 112 ms (dashed lines) [Rh 0.5: T_{out} = 758 °C, T_{max} = 827 °C; Rh 0.3: T_{out} = 750 °C, T_{max} = 824 °C; Rh 0.1: T_{out} = 750 °C, T_{max} = 829 °C].

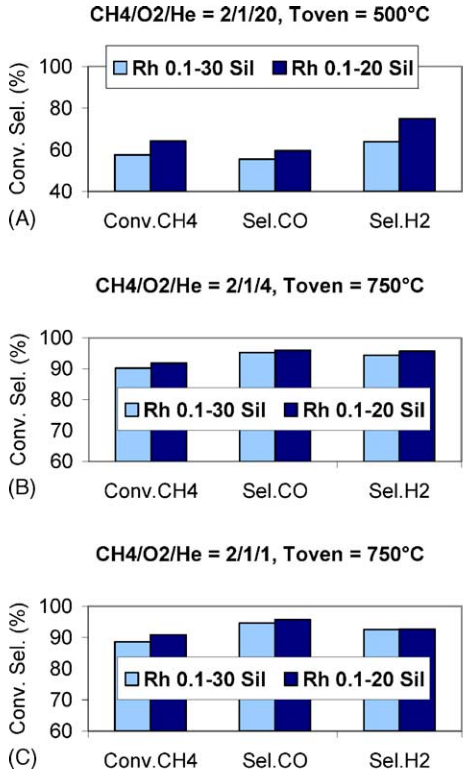

Fig. 4. Comparison of activity of ex-HT silicate catalysts Rh/Mg/Al 0.1/71/28.9 (a.r.) containing different excesses of silicate (20% or 30%); (A) reaction conditions: $CH_4/O_2/He = 2/1/20$, $T = 500$ °C, $\tau = 65$ ms [Rh 0.1 − 30% Sil: $T_{out} = 584$ °C, $T_{max} = 622$ °C; Rh 0.1 − 20% Sil: $T_{out} = 550$ °C, $T_{max} = 624$ °C]; (B) reaction conditions: $CH_4/O_2/He = 2/1/4$, $T = 750$ °C, $\tau = 65$ ms [Rh 0.1 − 30% Sil: $T_{out} = 769$ °C, $T_{max} = 828$ °C; Rh 0.1 − 20% Sil: $T_{out} = 763$ °C, $T_{max} = 847$ °C]; (C) reaction conditions $CH_4/O_2/He = 2/1/1$, $T = 750$ °C, $\tau = 112$ ms [Rh 0.1 − 30% Sil: $T_{out} = 750$ °C, $T_{max} = 829$ °C; Rh 0.1 − 20% Sil: $T_{out} = 770$ °C, $T_{max} = 842$ °C].

while the excess of 30% of silicates is more than that needed to inhibit the formation of the spinel and acts by also decreasing the amount of the MgO-type phase.

The XRD analyses were performed again on the samples tested in the laboratory plant (Fig. 1C) after more than 50 h of time on stream, no significant differences can be observed between the patterns before and after reaction, in accordance with the constant values of the surface area. The unchanged XRD and surface area is preliminary data that confirms the stability of these new materials. Furthermore the TGA analysis on the used catalyst excludes any coke formation during time on stream. Nevertheless to prove the stability of this catalyst the formation of coke and the loss of silica need to be investigated in more depth.

4. Conclusion

New nano-structured catalysts obtained from hydrotalcite-type precursors have been synthesised as catalyst for the catalytic partial oxidation of methane. The insertion of silicates instead of carbonates as interlayer anion affect the derived structure both before and after calcination. The silicates remain in the structure forming a new phase characterised by mixed silicate with a forsterite-type structure having formula $Mg_{2-x}M_{2/3x}SiO_4$ (M = Al, Rh), together with a MgO-type structure, but no Spinel-type phase was observed. The calcined samples presented high surface area values ($100\ m^2\ g^{-1}$) also after reaction, confirming the high thermal and mechanical stability of the materials.

The new catalyst presents higher CH_4 conversion and CO and H_2 selectivity with respect to that with the same formulation, but obtained from an HT containing carbonates, in which the spinel-type phase was present. The decrease in the amount of Rh, from 0.5 to 0.3 and 0.1, leads to slightly lower activity. By decreasing the amount of silicate inserted in the structure, a sample was obtained (Rh 0.1 a.r.) characterised by an increased amount of MgO phase with respect to the forsterite-type phase giving rise to significantly higher methane conversion and syngas selectivity with respect to the catalyst with Rh 0.1–30 Sil and the catalyst prepared using carbonate and having a Rh amount five times higher. These results can be attributed to the maximisation of the MgO phase in which the Rh can be soluted giving rise to high active and selective species and the absence of the spinel phase obtained with the silicate samples.

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