Partial oxidation of methane to synthesis gas over Rh-hexaaluminate-based catalysts

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The partial oxidation of methane to synthesis gas over catalysts consisting of Rh supported on hexaaluminates ($BaAl_{12}O_{19}$, $CaAl_{12}O_{19}$ and $SrAl_{12}O_{19}$) was investigated at atmospheric pressure and high reactant dilution in order to compare their performances within the kinetic-controlling regime. Comparison with the results obtained over a commercial Rh/α-Al_2O_3 system indicates that hexaaluminate catalysts are active and selective in this reaction. Despite of the higher surface area of the support, hexaaluminate-supported catalysts were found less stable, active and selective than an α-Al_2O_3-supported catalyst.

Keywords: partial oxidation of methane, rhodium catalyst, hexaaluminate-based materials, synthesis gas

1. Introduction

In the last years the interest in synthesis gas production via the process of catalytic partial oxidation of methane is increased. Various supported mixed oxides and noble metals have been reported to be active and selective to CO/H_2 mixture for this reaction [1–21].

In particular Rh supported over several oxides has been found to be active and selective to CO and H_2 (yield >80%) in the partial oxidation leading to conversion of methane close to the thermodynamic equilibrium values under certain operating conditions [1,2,14]. Also, over Rh no macroscopic carbon deposition or catalyst deactivation was observed [21].

Rh-impregnated gauzes, extruded or foam monoliths were studied as catalysts for the partial oxidation of methane by Schmidt and co-workers at extremely short residence times (10^{-4}–10^{-2} s) under adiabatic conditions [10–13]. Very high selectivity to synthesis gas (>90%) with almost complete conversion of methane was observed.

For this process two reaction paths have been proposed: the first is the sequence of complete oxidation followed by steam and dry reforming reactions and water–gas shift reaction ((1)–(4)); the second is the direct conversion of methane to CO and H_2 (reaction (5)):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -801.7 \text{ kJ/mol} \quad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H = 206.1 \text{ kJ/mol} \quad (2)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H = 247.5 \text{ kJ/mol} \quad (3)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H = 41.4 \text{ kJ/mol} \quad (4)$$

$$CH_4 + (1/2)O_2 \rightarrow CO + 2H_2 \quad \Delta H = -35.5 \text{ kJ/mol} \quad (5)$$

The identification of the actual reaction pathway as well as the analysis of the performances of different catalysts in the catalytic partial oxidation of methane is a demanding task. In view of the severe operating parameters of the process, experimental conditions can hardly be controlled. Uncertainties on catalyst temperature measurements are a debated issue in the literature and can result in a misleading evaluation of the thermodynamic constraints [3,4]. Besides, under such extreme conditions several catalysts were reported to provide very similar performances being conversion and selectivity governed by thermodynamic constraints [1,2].

To overcome these problems different experimental approaches have been proposed.

To control the temperature gradients in the catalyst bed Boucouvalas et al. [14,15] operate with high dilution of both the catalyst bed and the reactants. They performed their experiments with high space velocity in order to guarantee conversions significantly lower than those expected at thermodynamic equilibrium. Although such conditions are far from those relevant to practical applications, they allow for a fair comparison of catalytic performances between different catalysts. Also, the transient pulse technique was used to compare the performances of different catalysts since feeding little pulses of reactants to the reactor could minimize the hot spots [22,23].

In this work supported Rh catalysts were investigated aiming at a comparison of the catalytic performances depending on the support material. Particularly, catalysts consisting of Rh supported over hexaaluminate-based materials Rh/$BaAl_{12}O_{19}$, Rh/$CaAl_{12}O_{19}$ and Rh/$SrAl_{12}O_{19}$, were tested in the partial oxidation of methane and compared with Rh/α-Al_2O_3. Indeed the hexaaluminate supports, largely studied and employed in the catalytic combustion process, were proven to be extremely resistant to sintering at high temperature, retaining surface areas near to 10 m^2/g after prolonged heating at 1600 °C [24]. This appears a promising feature for the catalytic partial oxidation process under severe temperature conditions.

The experiments have been carried out with short contact time and diluted reacting mixture and catalytic bed. Such operating conditions have been chosen to minimize T-gradients in the reactor and the role of diffusion limitation and to reduce the impact of thermodynamic constraints in order to operate under kinetic-controlled regime, thus allowing a fair comparison of the different catalysts.

Supported catalysts have been also characterized by means of BET, XRD in order to provide insight into the observed reaction performances.

2. Experimental

2.1. Catalyst preparation

$BaAl_{12}O_{19}$ and $SrAl_{12}O_{19}$ were prepared in our laboratory using a method based on coprecipitation in aqueous medium by addition of $(NH_3)_2CO_3$ [25]. The support $CaAl_{12}O_{19}$ was prepared via the sol–gel method and provided by Enitecnologie [26], whereas α-Al_2O_3 is a commercial material (Aldrich).

The samples were dried and then calcined at 1573 K for 10 h (heating rate = 60 K/h, cooling rate = 100 K/h).

Rh 0.5% w/w was deposed onto all the supports by dropping at room temperature a red n-hexane solution of $Rh_4(CO)_{12}$ [27] (prepared as reported by Chini et al. [28]) into a slurry of the powdered supports in the same solvent. Reaction between the precursor and oxide surfaces caused an immediate decoloration of the red solution. The slurry was aged for 4 h, then filtered and dried.

Before testing in CPO experiments all the catalysts were treated in reaction atmosphere up to 300 °C.

2.2. Characterization

XRD analyses were performed with a Philips PW 1050–70 vertical goniometer using Ni-filtered Cu Kα radiation. XRD spectra of fresh samples were compared with reference diffractograms reported in literature in order to verify the formation of the desired phase [29]. XRD analyses of the catalysts after the activity tests were performed as well.

Surface areas were measured according to the BET method with a Carlo Erba Sorptomatic 1900 series instrument.

2.3. Catalytic activity tests

Catalytic tests were carried out in a quartz microreactor with an internal diameter of 8 mm. The reactor was placed inside an electric furnace equipped with an electric heater driven by a proportional-integral-derivative (PID) electronic temperature controller. Small amounts of fine catalyst in powders (50 mg with a particle size of 90 μm) diluted with commercial and extremely pure α-Al_2O_3 (Aldrich) with identical particle size in ratio 1/5 wt/wt were used (catalyst bed length = 4 mm). The catalyst was held in the reactor tube by means of α-Al_2O_3 (20–35 mesh) and quartz wool plugs. The temperature of the catalytic bed was monitored with a K-type thermocouple sliding inside a quartz well (i.d. = 1 mm, o.d. = 2 mm) inserted in the catalytic bed. N_2, O_2 and CH_4 were fed separately to the reactor from gas cylinders and were premixed before entering the catalyst bed.

Reactants and products were analyzed on-line by using a Hewlett–Packard gas chromatograph (6890 series 1). A molecular sieves HPPLOT 5A capillary column connected to a thermal conductivity detector (TCD) was used to separate O_2, H_2, N_2, CH_4 and CO whereas an in parallel Poraplot Q (HPPLOTQ) capillary column connected to a TCD was used to analyze CO_2, H_2O and hydrocarbons. C, H and O balances always closed within ±5%.

All the experiments were conducted with a gas hourly space velocity (GHSV) of 500,000 $l(NTP)/(h\,kg_{cat})$ (total flow rate = 420 Ncm^3/min) with a $CH_4/O_2/N_2$ molar feed ratio of 2/1/47 at a total pressure of 1–1.2 atm depending on pressure drops in the catalyst bed. The high degree of dilution of reactants with N_2 and the dilution of the catalyst with inert α-Al_2O_3 allowed to minimize hot spots in the catalytic bed.

During the activity tests (over Rh-hexaaluminate-based catalysts), reaction temperature was varied in the range 700–1250 K. Also, experimental tests without catalyst were performed in order to evaluate the role of homogeneous reactions. At the highest temperatures ($T > 1100$ K) C_2-hydrocarbons were present only in negligible amount in the product mixture.

3. Results and discussion

3.1. Catalyst characterization

In the case of fresh hexaaluminate-supported catalysts XRD analyses indicate that monophasic materials with β-alumina structure were formed upon calcination at 1300 °C. The presence of Rh was not revealed by XRD spectra possibly due either to the low Rh content (0.5% w/w) or to high dispersion of Rh species. Also, in the case of the Rh/α-Al_2O_3 sample only reflections of α-Al_2O_3 were detected in the XRD spectrum.

Results of surface area measurements over the different catalysts are summarized in table 1. In line with previous literature studies [24], hexaaluminate type supports

Table 1
Surface areas of the supports.

Support	Surface area (m^2/g)
α-Al_2O_3	4
$BaAl_{12}O_{19}$	15
$SrAl_{12}O_{19}$	10
$CaAl_{12}O_{19}$	9

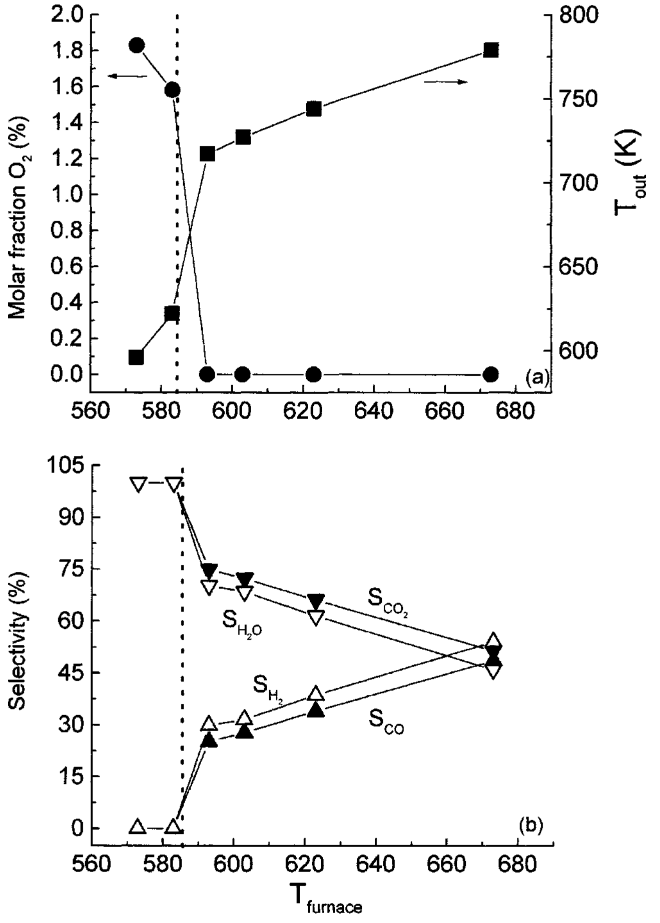

Figure 1. O_2 consumption and outlet temperature (a) and CO, CO_2, H_2 and H_2O selectivity (b) measured during the light-off over Rh/α-Al_2O_3.

maintain relatively high surface area upon calcination at 1300 °C. Values ranging from 10 to 15 m^2/s have been measured depending on the support, well above the value of 4 m^2/s obtained with commercial α-Al_2O_3 (calcination temperature = 1600 °C).

3.2. Activity tests

3.2.1. General features of reactor behaviour

It is known in literature that Rh/α-Al_2O_3 is active and selective in the catalytic partial oxidation of methane to synthesis gas [14,15]. Thus, it has been chosen as reference catalyst in our experiments. Activity tests were performed over this catalyst at increasing furnace temperature. It is worth describing the behaviour of this catalyst during the light-off. In figure 1(a) the oxygen outlet concentration and the outlet temperature are reported on increasing furnace temperature during the light-off. For temperature below a critical threshold of methane activation only low O_2 conversions (15%) and very low methane conversions (<5%) are observed. Above such threshold temperature ignition occurs characterized by total O_2 consumption, CH_4 conversion above 30% and increase of the outlet temperature up to 700–750 K, i.e., 80–100 K above the furnace temperature. Such behaviour has been observed over all the investigated catalysts. Accordingly, the ignition temperature has been used as a characteristic parameter of the activity performances in the catalyst screening.

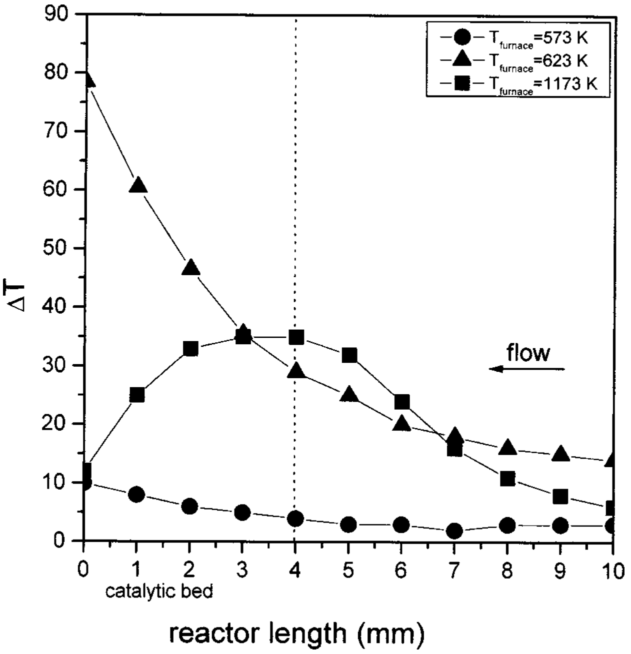

Figure 2. Temperature profiles versus reactor length measured at $T < T_{\mathrm{ignition}}$ (●), $T \geqslant T_{\mathrm{ignition}}$ (▲) and $T \gg T_{\mathrm{ignition}}$ (■). Operating conditions: $CH_4/O_2/N_2$ = 4/2/94 vol%, GHSV = 500,000 Ncm^3/(h g_{cat}), $P = 1$ atm.

Below the ignition temperature ($T_i \approx 620$ K) with low CH_4 and O_2 conversions, only CO_2 and H_2O were detected in the products as shown in figure 1(b), where CO, H_2, CO_2 and H_2O selectivity are reported on increasing the furnace temperature. Above the ignition temperature massive amounts of CO, H_2, CO_2 and H_2O are simultaneously detected in the products. Figure 1(b) also shows that the selectivity to CO and H_2 increased with the furnace temperature.

Despite of the high dilution of both the feed stream (94 vol% of N_2) and the catalyst (catalyst/inert = 1/5), significant axial temperature gradients have been measured in the catalytic bed. In figure 2 the axial profiles of the difference between the temperatures along the catalytic bed with and without reaction (ΔT) measured, below the light-off temperature (T_{furnace} = 573 K), at a temperature slightly higher than the ignition temperature (T_{furnace} = 622 K) and at a temperature much higher than the light-off (T_{furnace} = 1173 K) are reported. The maximum ΔT recorded below the light-off temperature was about 10 K, whereas upon methane ignition the maximum ΔT increased up to 80 K. The ΔT decreased in the experiments at higher temperature and the profiles became flatten, as expected from thermodynamics, on increasing CO/H_2 selectivity. It is worth noting that a maximum is evident in the ΔT profiles collected at high temperature and CH_4 conversion as a result of a step temperature increase followed by gradual temperature decrease. Such a maximum was, however, much less pronounced during tests over the Rh/hexaaluminates.

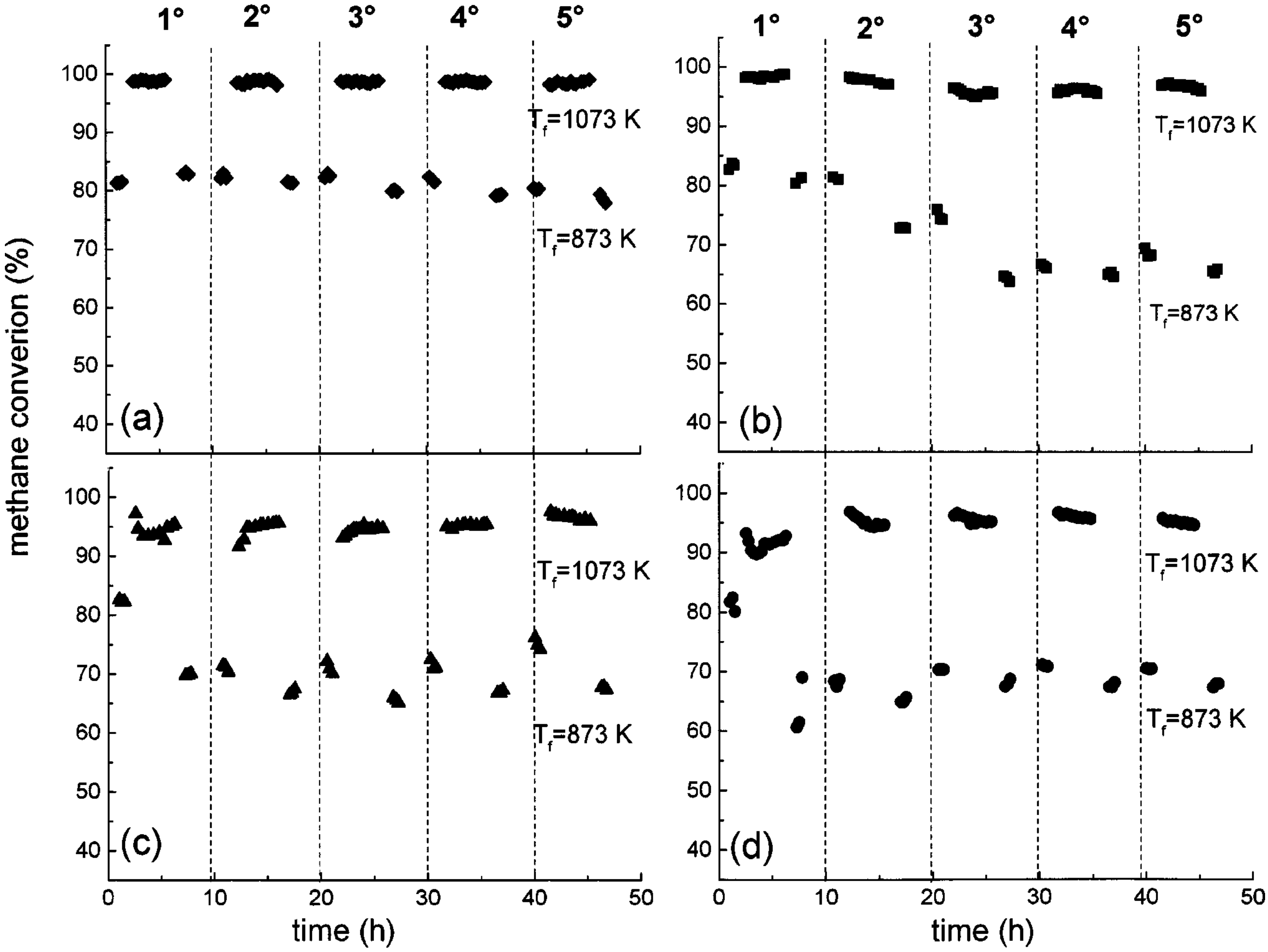

Figure 3. Effect of the conditioning on the methane conversion obtained over Rh/α-Al_2O_3 (a), Rh/$SrAl_{12}O_{19}$ (b), Rh/$CaAl_{12}O_{19}$ (c) and Rh/$BaAl_{12}O_{19}$ (d). Equilibrium values are reported with the dashed line. Operating conditions: $CH_4/O_2/N_2$ = 4/2/94 vol%, GHSV = 500,000 $Ncm^3/(h\,g_{cat})$, $P = 1$ atm.

The temperature profiles show that the experimental system is not able to disperse heat in order to guarantee isothermal conditions. Indeed the measured outlet temperatures were well consistent with enthalpy balance assuming that only 1/3 of reaction heat is dispersed. In view of such good consistency of enthalpy balances, the measured temperature can be considered representative of the catalyst one, thus the outlet temperature measured at the bottom of the catalytic bed was consistently used for computing thermodynamic constraints.

3.2.2. Conditioning of the catalysts

The fresh catalysts need to be conditioned in order to obtain reproducible results: indeed it was observed a continuous decrease of CH_4 conversion during time on stream in preliminary activity tests. After several attempts it was decided to maintain the catalyst at very high temperature (furnace temperature = 1073 K) for about 4 h monitoring, the methane conversion at a furnace temperature of 873 K and heating again at 1073 K for other 4 h and so on. The conditioning was considered finished when constant methane conversion with time on stream was achieved. Figure 3 shows the results obtained during the conditioning of the catalysts. A decrease of CH_4 conversion (corresponding to decrease in CO/H_2 selectivity) can be observed over all the hexaluminate-supported catalysts whereas Rh/α-Al_2O_3 maintains constant CH_4 conversion for all time of the conditioning (about 50 h).

The reproducibility of the conditioning behaviour of Rh/α-Al_2O_3 and Rh/$BaAl_{12}O_{19}$ was investigated by repeating the same treatment over different samples obtained from the same preparation batch. With Rh/α-Al_2O_3 essentially the same behaviour was obtained in repeated tests, whereas marked variations were observed with Rh/$BaAl_{12}O_{19}$, as shown in figure 4, where data of methane conversion at 873 and 1073 K versus time on stream are reported. Upon 40 h of conditioning, CH_4 conversion ranging from 40 to 60% at 873 K and from 75 to 90% have been obtained depending on the sample.

Conversion decrease with time on stream as well as difficulties in reproducing conditioning provided evidence on a certain instability of the hexaaluminate-based materials in the partial oxidation process.

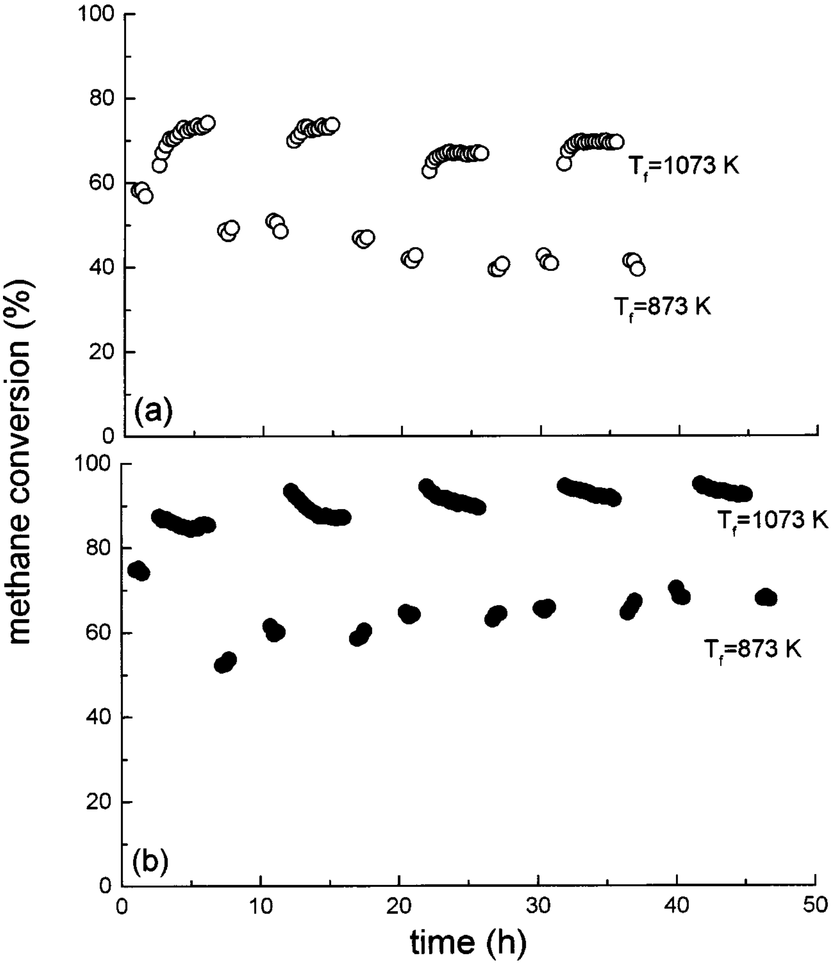

Figure 4. Effect of the conditioning on the methane conversion obtained over two samples of Rh/$BaAl_{12}O_{19}$. Equilibrium values are reported with the dashed line. Operating conditions: $CH_4/O_2/N_2 = 4/2/94$ vol%, GHSV = 500,000 $Ncm^3/(h\, g_{cat})$, $P = 1$ atm.

The reason of this instability shown during activity tests is still unclear but further investigation will be undertaken. An incorporation of noble metal in the hexaaluminate structure could be responsible of this activity decrease during conditioning and of worse light-off and selectivity performances. Incorporation of Rh in spinel-type structure was observed by Basile et al. in CPO Rh-containing catalysts [30]. At high temperature the hexaaluminate can easily incorporate transition metal ions in the structure [24]. Despite of the much larger ionic radius of Rh^{3+} (0.67 Å [31]) than those of transition metal ions the incorporation phenomena cannot be excluded.

XRD spectra of the sample before and after activity tests (including conditioning) do not show any significant differences (e.g., enlargement of cell parameter) associated with Rh^{3+} incorporation. However, due to the very limited amount of Rh in the sample this phenomenon cannot be taken as a proof that incorporation has not occurred.

3.2.3. Comparison of the supported catalysts

After conditioning, the catalyst comparison was performed by testing the catalysts supported over the different oxides under the operating conditions that were demonstrated to guarantee operation under kinetic-controlled regime.

Before showing and discussing the results, some preliminary consideration on the role of diffusional limitations can be inferred from data shown previously. In the experiments very small particle size (90 μm) was adopted to minimize the effect of mass and heat transport processes. Despite of this, the role of diffusional limitations cannot be excluded: in fact, as described above (figure 1), it was not possible to control the O_2 conversion after the light-off so that no data on consumption rate of O_2 can be obtained in order to perform theoretical evaluation on the role of diffusion. On the other hand, when considering the rate of formation of the desired products (CO and H_2) *a posteriori* criteria on the absence of the diffusional limitations are widely satisfied [32]. Accordingly, it can be assumed that the production of such species is governed by chemical kinetics. This allows for a fair comparison of the different supported catalysts based on methane conversion and selectivity performances.

The activity tests showed different ignition temperatures depending on the catalyst, as reported in table 2. The results proved that the Rh/α-Al_2O_3 catalyst is the most active

Table 2
Ignition temperature for the catalysts.

Catalyst	Ignition temperature (K)
Rh/α-Al_2O_3	620
Rh/$BaAl_{12}O_{19}$	750–825
Rh/$SrAl_{12}O_{19}$	653
Rh/$CaAl_{12}O_{19}$	660

among the investigated catalysts, its ignition temperature of 620 K being 30 K lower than the lowest temperature measured over hexaaluminate-supported catalysts. Rh/$SrAl_{12}O_{19}$ and Rh/$CaAl_{12}O_{19}$ exhibited similar light-off performances whereas Rh/$BaAl_{12}O_{19}$ is much less active showing an ignition temperature about 150–200 K higher than that obtained with the other catalysts.

The effect of temperature on the partial oxidation reaction was investigated by increasing temperature from 700 to 1250 K. Methane conversion and the selectivity to CO and H_2 are reported in figures 5 and 6, respectively, as a function of the temperature measured at the outlet of the catalytic bed. Values of conversion and selectivity from thermodynamic equilibrium are also reported in the same figures for the sake of comparison.

Figure 5 shows that a higher conversion of methane could be obtained over Rh/α-Al_2O_3 in the whole investigated range of temperature with respect to the other catalysts. Rh/$CaAl_{12}O_{19}$ showed a conversion of methane similar to Rh/α-Al_2O_3 up to 900 K, remaining lower for higher temperatures. The same behaviour was observed for Rh/$SrAl_{12}O_{19}$ and Rh/$BaAl_{12}O_{19}$. In the whole investigated range of temperature the conversion of methane remained below the thermodynamic equilibrium for all the studied catalysts, except at extremely high temperatures.

In line with mass balance considerations the higher CH_4 conversions observed over Rh/α-Al_2O_3 correspond to higher selectivity to CO and H_2 (figure 6) with respect to those obtained over the Rh/hexaaluminate-based materials. Rh/$CaAl_{12}O_{19}$, Rh/$SrAl_{12}O_{19}$ and Rh/$BaAl_{12}O_{19}$ showed a similar behaviour and similar performances. The following order of selectivity to CO/H_2 depending on the supports can be derived:

$$\mathrm{Rh}/\alpha\text{-}\mathrm{Al_2O_3} \geqslant \mathrm{Rh/CaAl_{12}O_{19}} \approx \mathrm{Rh/SrAl_{12}O_{19}} \approx \mathrm{Rh/BaAl_{12}O_{19}}$$

Such a series is well consistent with that observed for the order of light-off activity.

In line with CH_4 conversion data, at low temperature the selectivity to CO/H_2 was lower than the corresponding equilibrium data. The results also showed a gradual approach to equilibrium on increasing temperature. Above $T = 1050$ K the selectivity reached the value expected at thermodynamic equilibrium over Rh/α-Al_2O_3, Rh/$CaAl_{12}O_{19}$ and Rh/$SrAl_{12}O_{19}$, but not over Rh/$BaAl_{12}O_{19}$. The gradual approach to thermodynamic equilibrium suggests that CO and H_2 formation occurs, under the investigated conditions, via an indirect scheme, i.e., total combustion followed by reforming and shift reactions. Along these lines, the similarity between the ignition activity and the CO/H_2 selectivity can be explained by assuming that the Rh/α-Al_2O_3 catalyst, for reasons that are still unclear, is more active in both combustion and reforming reactions. Further investigations are currently in progress to better clarify this point.

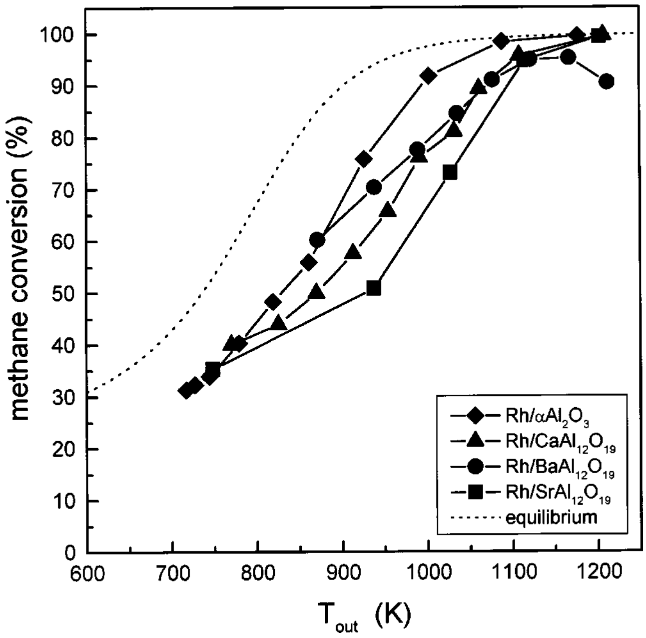

Figure 5. Effect of temperature on the conversion of methane over Rh/α-Al_2O_3, Rh/$CaAl_{12}O_{19}$, Rh/$SrAl_{12}O_{19}$ and Rh/$BaAl_{12}O_{19}$. Methane conversion values at thermodynamic equilibrium are reported with dashed line. Operating conditions: $CH_4/O_2/N_2 = 4/2/94$ vol%, GHSV $=$ 500,000 $\mathrm{Ncm^3/(h\,g_{cat})}$, $P = 1$ atm.

As a matter of fact, the results obtained during the activity tests as well as the behaviour observed during conditioning clearly demonstrate that Rh-based catalysts supported over hexaaluminates exhibit worse performances than those observed over Rh/α-Al_2O_3. Indeed higher light-off temperature and lower selectivity to CO and H_2 have been obtained under the former catalyst under peculiar investigated conditions. Besides poor stability of hexaaluminate-supported catalysts was evidenced by decrease of methane conversion with time on stream at 1073 K.

Such worse performances were obtained despite of high and stable surface area of hexaaluminates that was expected to improve dispersion of the supported Rh species.

The reason for this behaviour has not been clearly identified in this work. Rh–support surface interactions due to the basic properties of the different support materials could explain the differences observed in methane conversion and CO/H_2 selectivity (as shown in figures 5 and 6). Alternatively, the incorporation of Rh in the hexaaluminate structure, already cited in a previous paragraph, can result in lower amount of noble metal available for the reaction and, accordingly, in lower activity.

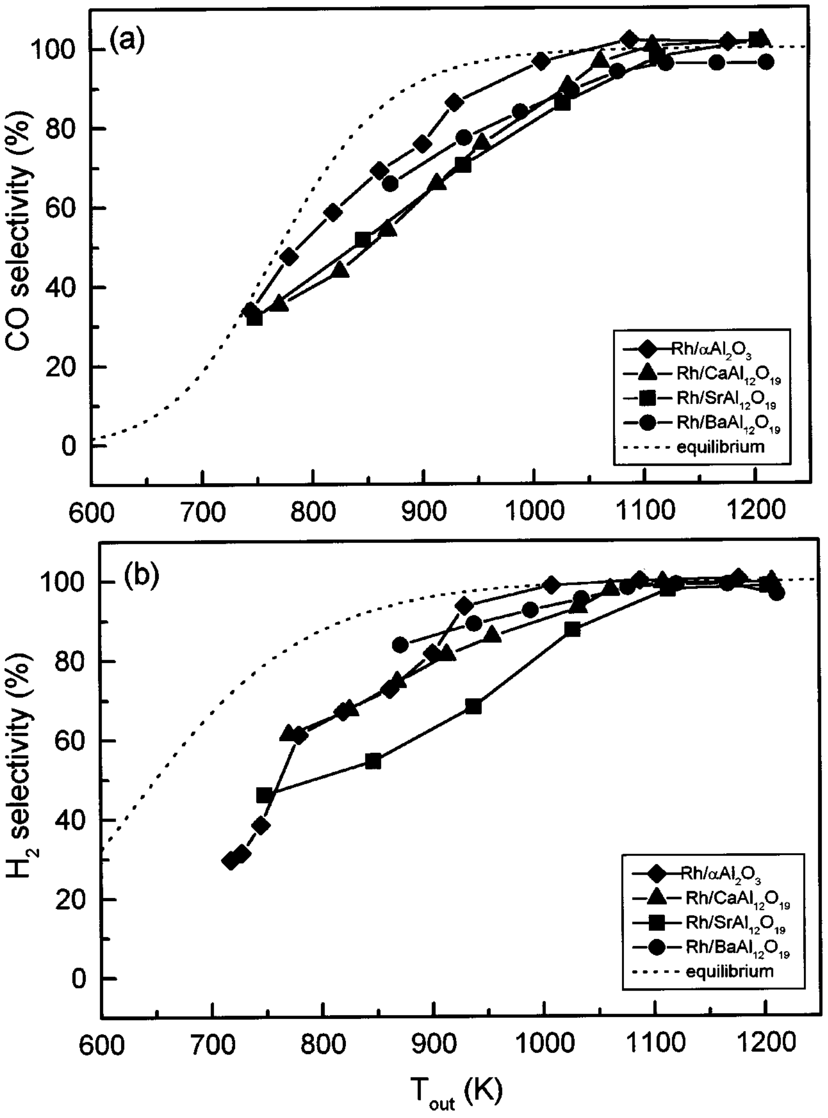

Figure 6. Effect of temperature on the selectivity to CO (a) and H_2 (b) over Rh/α-Al_2O_3, Rh/$CaAl_{12}O_{19}$, Rh/$SrAl_{12}O_{19}$ and Rh/$BaAl_{12}O_{19}$. Equilibrium values are reported with dashed lines. Operating conditions: $CH_4/O_2/N_2$ = 4/2/94 vol%, GHSV = 500,000 Ncm^3/(h g_{cat}), $P = 1$ atm.

4. Conclusions

The operating conditions used in the activity tests allowed working under chemical kinetic controlled regime. This permitted a fair comparison of the different supported catalysts based on conversion and selectivity performances.

Particularly, the following conclusions can be drawn from the results of the present study:

(1) The different Rh/hexaaluminate-based materials and the Rh/α-Al_2O_3 show the following order of activity: Rh/α-Al_2O_3 $>$ Rh/$CaAl_{12}O_{19}$ $\approx$ Rh/$SrAl_{12}O_{19}$ $\gg$ Rh/$BaAl_{12}O_{19}$, estimated by the measured ignition temperature.

(2) The results obtained in the range of temperature 900–1050 K reveal the same order of selectivity towards CO and H_2: Rh/α-Al_2O_3 $\geqslant$ Rh/$CaAl_{12}O_{19}$ $\approx$ Rh/$SrAl_{12}O_{19}$ $\approx$ Rh/$BaAl_{12}O_{19}$.

(3) The activity and selectivity performances of the catalysts supported on hexaaluminate type materials decrease during high-temperature conditioning under reaction atmosphere, whereas Rh/α-Al_2O_3 exhibits stable performances.

(4) The conversion of methane remained below the thermodynamic equilibrium in the range of temperature investigated for all the materials tested except at the high temperatures ($T > 1050$ K) where the conversion of methane reaches the 100% value over Rh/α-Al_2O_3, Rh/$CaAl_{12}O_{19}$ and Rh/$SrAl_{12}O_{19}$.

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