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Enthalpy recovery of gases issued from H_2 production processes: Activity and stability of oxide and noble metal catalysts in oxidation reaction under highly severe conditions

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Abstract

Oxidation activity and stability under reaction was investigated for a series of mixed oxide catalysts, doped or not by a precious metal (Pd, Pt). The reaction feedstock, containing CO, H_2, CH_4, CO_2 and H_2O, simulated gases issued from H_2 production processes for fuel cells. Contrarily to conventional noble metal catalysts, mixed oxide samples present generally good stability under reaction at high temperature. The activities measured for the perovskite and hexaaluminate catalysts, are however largely lower than that of the reference Pd/Al_2O_3 catalyst. High activities were obtained after impregnation of 1.1 wt.% Pd or 0.8 wt.% Pt on the hexaaluminates samples. Even if Pd/Al_2O_3 was found to present a high activity, this sample suffered from drastic deactivation at 700 °C. Better stability were obtained on perovskite. Furthermore, doping hexaaluminate by Pt led to samples with good activities and high stability. Even if better activities were obtained by doping the hexaaluminate samples by Pd, the $Pd/BaAl_{12}O_{19}$ strongly deactivated, as it was previously observed for the reference catalyst. Interestingly, this Pd deactivation was not observed when Pd was impregnated on the Mn substituted hexaaluminate, leading to a stable and active catalyst. This suggests that it is possible to stabilize the palladium in its oxidized form at high temperature (700 °C) on the surface of some supports.

Keywords: H_2 fuel cell; Oxidation reaction; Noble metals; Perovskites; Hexaaluminates; Stability; Activity

1. Introduction

Palladium and platinum supported catalysts are known to present high activities in oxidation reactions. Many reviews were devoted to the properties of noble metal-based catalysts [1–3]. Metal sintering and structural changes are major causes of deactivation of these catalysts in oxidation reaction at high temperature. Several metal oxide catalysts were then proposed for catalytic combustion, and have also been found to present high activities in oxidation reactions. Among the oxide catalysts, perovskite (of general formula ABO_3) and hexaaluminate ($BAl_{12}O_{19}$) were described as good candidates for reactions at high temperatures. For example, some authors [4,5] reported similar activities between transition metal-based perovskites (with Co and Mn in the B position) and Pt/Al_2O_3. Properties of transition metal-based perovskites in oxidation reactions [6–9], and especially relationship between oxygen mobility and activity [10–13], were then extensively studied during the past few decades. Barium hexaaluminate-based solids were also proposed as catalysts for catalytic combustion, since these solids maintained relatively high surface areas after calcination at high temperature [14]. Doping hexaaluminate samples by a transition metal [15,16], or by noble metal [17], also resulted in an increase in activity for the CH_4 oxidation reaction.

This work deals with the oxidation of the effluents issued from the ethanol steam reforming (ESR) within a global project of ESR in a membrane reactor coupled with a PEM fuel cell. The reforming reaction, and the H_2 separation, are performed on the noble metal membrane at a temperature higher than 600 °C. Nevertheless, ethanol conversion into hydrogen is rather incomplete, and results in the presence of H_2, CO, and CH_4 in the effluent gases. In order to minimize the process energy consumption, heat generated by the effluent combustion should be used to heat the reformer. This imply to develop combustion catalysts that are very active for the H_2, CO and

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CH_4 oxidation reactions and remain very stable at high reaction temperatures (typically 700–750 °C). Then, the aim of this work is to evaluate the activity and stability of some perovskite and hexaaluminate catalysts for the oxidation of a mixture of reducers (H_2, CO and CH_4) simulating gases issued from hydrogen production processes (other gaseous components: CO_2 and H_2O in N_2). The effect of doping hexaaluminate samples by Pt and Pd was also studied. The results obtained on the samples were compared to those obtained for a reference sample 1 wt.% Pd/Al_2O_3.

2. Experimental

2.1. Sample synthesis

Since transition metal-based perovskites were found to show interesting activities for the oxidation reactions [6], $LaCoO_3$ (LaCo) and $LaMnO_3$ (LaMn) perovskites were synthesized by the citrate complexation method, following the procedure described earlier [12]. Nitrate salts ($La(NO_3)_3{\cdot}6H_2O$, and $Co(NO_3)_2{\cdot}6H_2O$ or $Mn(NO_3)_3{\cdot}4H_2O$) were first dissolved in distilled water and mixed together. The solution was then slowly added to the citric acid first dissolved in water. Thereafter, the excess of water was slowly evaporated at ambient temperature under stirring until a vitreous gel was obtained. The so obtained gel was dried under vacuum at 80 °C for one night, and at 110 °C for 1 day. Finally, the powder was hand ground and calcined for 8 h at 750 °C (ramp = 2 °C/min).

$BaAl_{12}O_{19}$ (BaAl) and $BaMnAl_{11}O_{19}$ (BaMnAl) samples were synthesized according to the procedure described by Groppi et al. [15,16]. Nitrate precursors ($Ba(NO_3)_2$, $Mn(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$) were first dissolved in distilled water. After mixing, the pH of the resulting solution was adjusted at 1.0 by adding HNO_3. The solution was then slowly added under vigorous stirring to a solution of $(NH_4)_2CO_3$ in water at 60 °C. The pH was controlled to stay stable around 7.5–8.0 during the precipitation. Thereafter, the precipitate was aged at 60 °C for 3 h, filtered and thoroughly washed with distilled water for nitrate removal. The precipitate was dried one night at 110 °C, and then calcined at 1100 °C ($BaMnAl_{11}O_{19}$) or 1300 °C ($BaAl_{12}O_{19}$) for 10 h (ramp = 2 °C/min).

The hexaaluminate samples were impregnated with platinum and palladium. $Pd(NO_3)_2$ and $Pt(NH_3)_2(NO_3)_2$ in water were used as noble metal precursors. The solution containing the noble metal was slowly added to the hexaaluminate support. Excess of water was then slowly evaporated at 80 °C, and the solid dried at 120 °C for one night. The samples containing Pd (PdBaAl and PdBaMnAl) were finally calcined at 800 °C under air (20 mL/min, ramp = 3 °C/min). Pt doped samples (PtBaAl and PtBaMnAl) were calcined at 450 °C under air, reduced at 450 °C under H_2, and calcined at 800 °C under air (conditions: 20 mL/min, ramp = 3 °C/min).

2.2. Characterization

Sample composition was verified by ICP, using a P40 apparatus from Perkin-Elmer. Specific surface areas were calculated by applying the BET method to the nitrogen adsorption isotherms obtained at −196 °C on an Micromeritics ASAP 2000 instrument. Before nitrogen adsorption, the samples (0.35 g) were degassed 4 h at 200 °C. XRD spectra of fresh samples were collected on a SIEMENS D5000 diffractometer using a Cu Kα radiation. Spectra were recorded for 2θ values from 15° to 75° by 0.05° step with a duration step of 2.4 s.

2.3. Catalytic test

Catalyst activity was measured for the oxidation of a mixture composed of 17.6% O_2–2.9% CO_2–4.1% H_2O–1.5% CH_4–1.5% H_2–1.5% CO–bal N_2, which was proposed to simulate gases issued from H_2 production processes. For each test, a weight of 0.050 g of catalyst diluted in 0.250 g of carborundum was introduced in a U-shaped quartz microreactor between two quartz wool plugs. A reaction flow of 400 N mL/min, corresponding to a gas hourly space velocity of 240,000 h^{-1}, passed through the reactor. After stabilization of the flow rate, the test began with a temperature ramp of 10 °C/min from 40 to 700 °C. At 700 °C, heating was stopped, and the solid was quickly cooled down to room temperature (20 min). After 30 min at the ambient temperature, a second ramp (conditions as the first one) was performed. At the end of the second ramp, the temperature was stabilized at 700 °C, and the stability of the catalysts tested under reaction for 12 h. During the test, reactants and products were analyzed by gas chromatography (two TCD for H_2, CO, CO_2, O_2 and one FID for CH_4).

3. Results and discussion

3.1. Physical characterization

The physical properties of the synthesized samples are summarized in Table 1. XRD patterns obtained for LaCo and LaMn show pure perovskite phase after calcination at 800 °C (Fig. 1a and b and Table 1). The specific surface areas are however relatively low (6.2 m^2/g for LaCo and 8.3 m^2/g for LaMn). The BaAl sample presents specific surface area slighly lower than 10 m^2/g whereas BaMnAl presents a specific surface area of 44.6 m^2/g (Table 1). The surface area obtained for BaAl is comparable with that obtained by Groppi et al. [15] for $BaAl_{12}O_{19}$ (15 m^2/g). XRD patterns obtained by these authors are similar with those obtained for our samples (Fig. 1c and Table 1). Weak reflections attributed to α-Al_2O_3 and $BaAl_2O_4$ are detected, suggesting that 1300 °C is enough to convert the most important part of the precursors into hexaaluminate. Groppi et al. [15] and Artizzu-Duart et al. [18] reported however similar specific surface areas on Mn-doped hexaaluminates (15–20 m^2/g). In our case, the larger specific surface area obtained for BaMnAl than for BaAl can be attributed to the lesser extent of crystallization of the precursor into hexaaluminate, and the occurrence of an important fraction of $BaAl_2O_4$ in the final solid [15]. Impregnating BaAl and BaMnAl by a noble metal, either Pt (at 0.8 wt.%) or Pd (at 1.1 wt.%), results in a small decrease in specific surface area (Table 1).

Table 1
Physical properties of the catalysts

Sample	Synthesis method	Chemical composition[a]	Treatment temperature[b] (°C)	DRX[c]	S_{BET} (m^2/g)
LaCo	Citrate	$LaCo_{0.96}O_3$	c 750	P Co	6.2
LaMn	Citrate	$LaMn_{0.98}O_3$	c 750	P Mn	8.3
BaAl	Carbonate	$Ba_{0.64}Al_{12}O_x$	c 1300	Weak α and Ba, H	9.9
PdBaAl	Impregnation	1.1% $Pd/Ba_{0.64}Al_{12}O_x$	c 1300 − c 800	n.a.	9.3
PtBaAl	Impregnation	0.8% $Pt/Ba_{0.64}Al_{12}O_x$	c 1300 − c 450 − r 450–c 800	n.a.	9.3
BaMnAl	Carbonate	$Ba_{0.68}Mn_{0.67}Al_{11}O_x$	c 1100	Weak α, Ba, H	44.6
PdBaMnAl	Impregnation	1.1% $Pd/Ba_{0.68}Mn_{0.67}Al_{11}O_x$	c 1100 − c 800	n.a.	34.5
PtBaMnAl	Impregnation	0.8% $Pd/Ba_{0.68}Mn_{0.67}Al_{11}O_x$	c 1100 − c 450 − r 450 − c 800	n.a.	35.8

[a] Chemical composition obtained by ICP.
[b] c, calcined under air (20 mL/min); r, reduced under pure hydrogen (20 mL/min).
[c] Crystallographic phases detected in the XRD patterns: P Co, $LaCoO_3$ (JCPDS file no. 48–1023), P Mn, $LaMnO_{3.15}$ (JCPDS file no. 50–0298), α, α-Al_2O_3 (JCPDS file no. 10–0173), Ba, $BaAl_2O_4$ (JCPDS file no. 17–0306), H, Ba-β-Al_2O_3 (JCPDS file no. 33–0129).

3.2. Activity

Light-off temperatures ($T_{10\%}$, temperature at 10% conversion) for the CO, H_2 and CH_4 oxidation are summarized in Fig. 2. Large differences are observed among the samples. Light-off curves obtained on the first oxidation cycle showed slightly higher activity for LaCo than for LaMn (Figs. 2 and 3), even if LaMn shows a higher specific surface area than LaCo. Both the perovskite samples present a shoulder in the H_2 oxidation curve, suggesting that this reaction becomes mass transfer limited above 380 °C [20]. Hexaaluminates samples (BaAl and BaMnAl) present lower activities than the two perovskites. This is clearly observed by comparing temperatures at 10% conversion obtained for BaAl and the two perovskite samples (Fig. 2). Ten percentage of methane conversion is hardly attained on BaAl at 700 °C, whereas this conversion is reached at 560, 580 and 675 °C on LaCo, LaMn and BaMnAl, respectively. Then, substituting an hexaaluminate with manganese (BaMnAl) permitted to increase significantly the activity of the hexaaluminate. The increase in activity observed for the methane oxidation reaction is also observed for CO and H_2 oxidation rates (Fig. 2). Since manganese oxide was found to present a high activity in oxidation reaction [19], the increase in activity can be attributed to the redox properties of the transition metal, which gave a solid with an activity only slightly lower than those obtained for the two perovskites, but largely higher than the activity of unsubstituted BaAl (Fig. 3).

Doping hexaaluminate samples by noble metal results in a significant decrease of the light-off temperatures (Fig. 2). For PtBaMnAl, CO and H_2 are completely oxidized into CO_2 at 244 and 220 °C, respectively. For PdBaMnAl, temperatures of complete conversion of CO and H_2 are 158 and 144 °C. These temperatures are clearly lower than the temperatures obtained for BaMnAl (484 °C for 100% CO conversion and 694 °C for 100% H_2 conversion). The effect on the CH_4 oxidation rate is less than for the CO and H_2 oxidation rate (Figs. 2 and 3). An increase in activity is however observed, specially for the PdBaMnAl sample which shows a methane conversion higher than 80% at 700 °C whereas BaMnAl shows only 32% conversion at this temperature. Similar observations are made

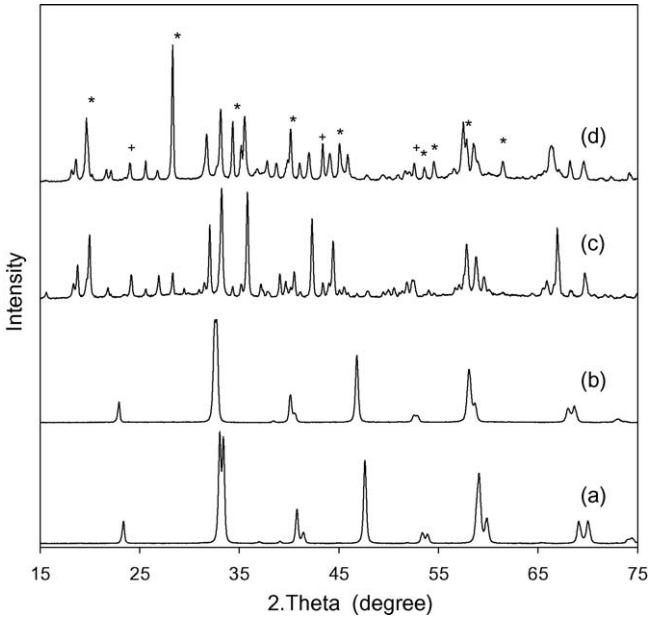

Fig. 1. XRD patterns obtained for: (a) LaCo; (b) LaMn; (c) BaAl; (d) BaMnAl. (*) $BaAl_2O_4$; (+) α-Al_2O_3.

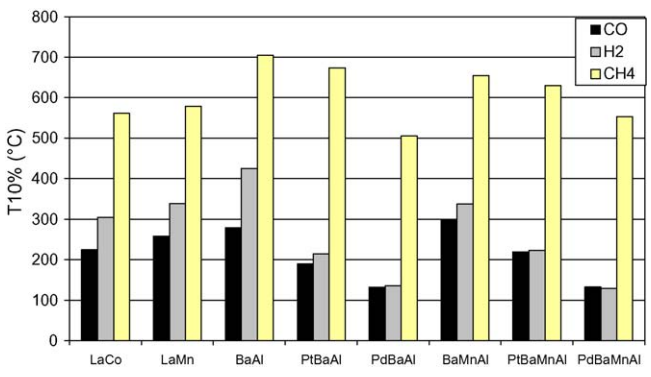

Fig. 2. Temperature of 10% conversion obtained for the CO, H_2 and CH_4 oxidation reaction on the different samples.

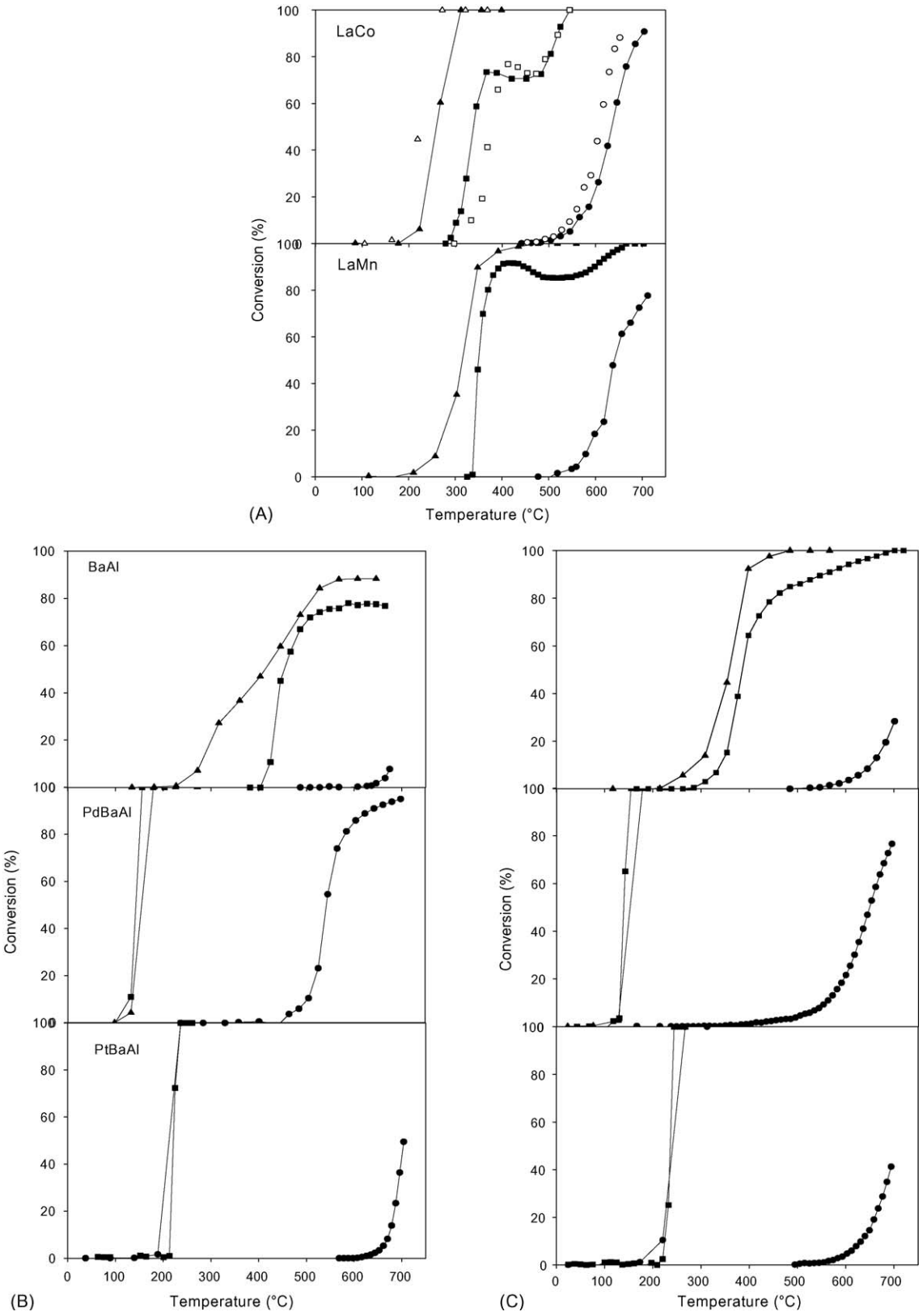

Fig. 3. Light-off curves obtained for the oxidation reaction during the first oxidation cycle. (▲) CO conversion; (■) H_2 conversion; (●) CH_4 conversion. Open symbol: second oxidation cycle. (A) Perovskites; (B) BaAl based samples; (C) BaMnAl based samples.

when BaAl was impregnated by Pt or Pd. Whereas the activity of BaAl for the CH_4 oxidation reaction starts at 700 °C ($x_{CH_4} = 8\%$ and 700 °C), CH_4 conversions of 49 and 95% were obtained on PtBaAl and PdBaAl at the same temperature. Temperatures for 10% CO conversion and H_2 conversion are similar for the BaAl and BaMnAl doped samples. This suggests that the support plays a minor role in comparison with the noble metal in the low temperature oxidation reactions (like CO and H_2).

In this work, we clearly observed that doping hexaaluminates with noble metals has a stronger effect with Pd than with Pt (see Figs. 2 and 3B and C). Supported Pd catalysts are however known to be the most active materials, especially in the total oxidation of methane [2]. Recently, Kusar et al. [22] also reported higher activity of 2% $Pd/MgAl_2O_4$ than 2% $Pt/MgAl_2O_4$ for the CH_4 oxidation reaction. Similar orders of activity were obtained by these authors in the case of the catalytic combustion of gasified refuse-derived fuel (containing H_2, CO, CH_4 and C_2–C_{12} hydrocarbons). Interestingly, Kusar et al. [22] noticed there was a strong effect of the noble metal on the catalytic activity for H_2 and CO oxidation, while the methane activity remained low. Nevertheless, Sekizawa et al. [21] and Jang et al. [17] reported a net increase of the CH_4 combustion activity by doping different hexaaluminates ($Sr_{1-x}La_xMnAl_{11}O_{19}$) by Pd. These results suggest that the nature of the support may have a marked effect on the catalytic activity of Pd for the CH_4 conversion. It is however difficult, from our results, to discuss on the role of the support, and on the role of the interaction between support and noble metal on the catalytic activities.

The activities obtained for the samples synthesized in this work are however lower than the activity of the reference catalyst 1.0 wt.% Pd/Al_2O_3 which shows complete conversion of CO, H_2 and CH_4 at 118, 148 and 615 °C, respectively (not shown). Nevertheless, alumina support presents a specific surface area of 148 m^2/g after calcination at 750 °C. This is largely higher than the specific surface areas developed by the hexaaluminate samples (9.9 m^2/g for BaAl and 44.6 m^2/g for BaMnAl). The large difference in specific surface area between the hexaaluminate supports and the Al_2O_3 reference support can logically explain the higher activity observed for the reference sample (increase in dispersion of the active phase).

3.3. Stability

The thermal shock (first temperature ramp followed by a quick decrease of the reactor temperature until the room temperature) does not strongly affect the catalytic activity of the samples (see open symbol on LaCo, Fig. 2). Small differences are observed in the conversions measured for the two successive ramps. However, these differences cannot be considered as representative of a catalyst activity change since the conversions are not obtained in stationary regime but under dynamic conditions. These conditions also explain why some differences are observed between the CH_4 conversions obtained at 700 °C at the end of the ramp and at the beginning of the stability test (after 10 min of temperature stabilization).

During the stability test at 700 °C, large differences can be observed between the samples (Fig. 4). First of all, the reference

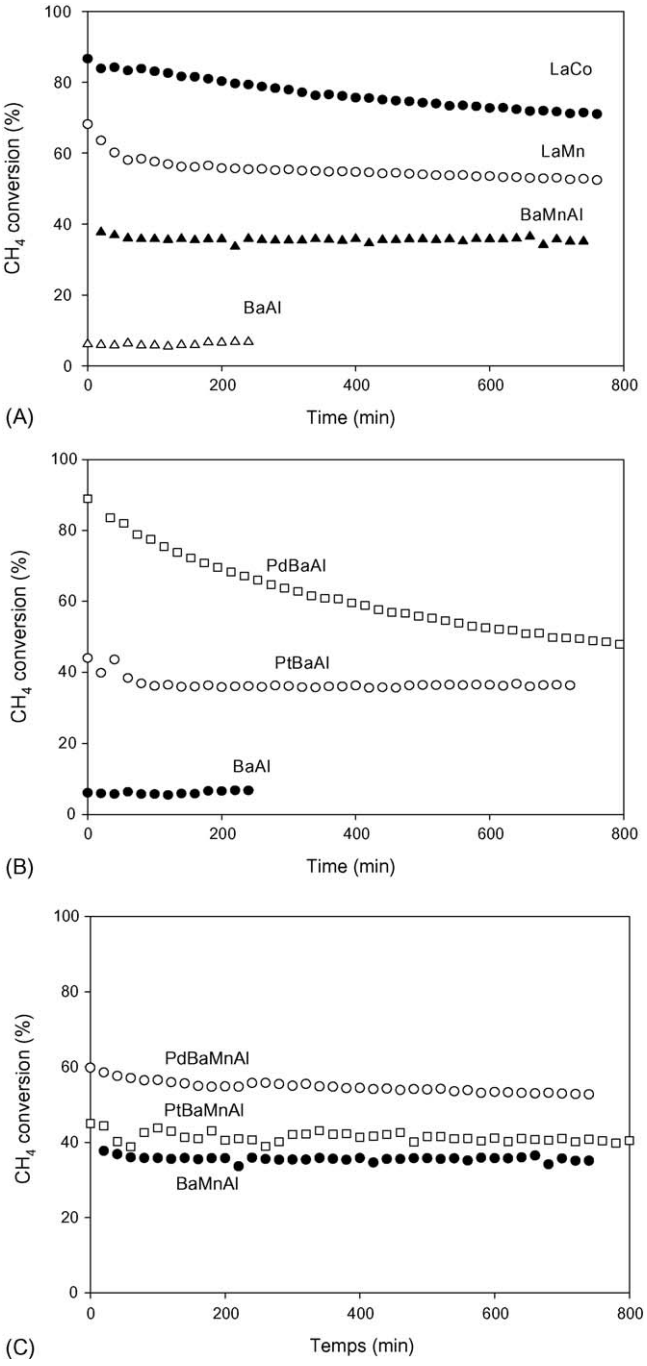

Fig. 4. Stability of the CH_4 conversion vs. time on stream: (A) comparison between the oxide catalysts; (B) effect of doping BaAl by a noble metal; (C) effect of doping BaMnAl by a noble metal.

sample Pd/Al_2O_3, which showed the highest activity, strongly deactivate under reaction conditions. The CH_4 conversion decreased from 100% at $t = 0$ h to 60% at $t = 12$ h (not shown).

Mixed oxide samples all exhibit a better stability than the reference catalyst. Perovskites shows moderate deactivation (CH_4 conversion obtained on LaCo decreases from 87 to 72% after 12 h, Fig. 4A). Nevertheless, after 12 h under reaction LaCo presents a higher CH_4 conversion than Pd/Al_2O_3, whereas LaMn presents a similar CH_4 conversion. The two hexaaluminates show very good stability, even though the CH_4

conversions obtained for BaAl and BaMnAl stay lower than those obtained for the perovskites and the reference catalyst after deactivation.

It was previously mentioned that doping hexaaluminates by noble metals resulted in an increase in catalytic activity. As for Pd/Al_2O_3, PdBaAl was found to strongly deactivate during the stability test. This can be attributed to a slow reduction of PdO into Pd^0 during the test [21]. This deactivation was not observed for PdBaMnAl, showing that certain supports can stabilize palladium in its oxidized form. For Pt-based samples, neither PtBaAl nor PtBaMnAl was found to deactivate. This allow us to conclude that metallic platinum, most active form of Pt in oxidation reaction, is stable under these reaction conditions and does not sinter.

4. Conclusion

Perovskite and Mn substituted hexaaluminate catalysts were found to be active for the oxidation of CO, H_2 and CH_4. The catalytic activities measured for the oxidation of gases issued from H_2 production processes (containing CO, H_2, CH_4, H_2O and CO_2) are however largely lower than that of a conventional 1.0 wt.% Pd/Al_2O_3 catalyst. Nevertheless, oxide catalysts show better stability under reaction than the reference catalyst which deactivates by progressive reduction of PdO into Pd^0 under reaction flow. Doping hexaaluminates by Pd or Pt results in a significant increase in activity, especially for the CO and H_2 oxidation reaction. It was also observed that PdBaMnAl was stable under reaction, suggesting that it is possible, by an adequate choice of the support, to stabilize palladium in its oxidized form at high temperature. This allows to obtain a catalyst which presents low light-off temperatures and high stability under reaction.

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