

Reforming of CH₄ with CO₂ on Pt-supported catalysts Effect of the support on the catalytic behaviour

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Abstract

This paper reports a study about the behaviour of different Pt-based catalysts supported on Al₂O₃, Na–Al₂O₃, K–Al₂O₃ and ZrO₂ in methane reforming with CO₂. Results indicate that Pt/Na (0.3 wt%)-Al₂O₃ and Pt/ZrO₂ catalysts show both a good activity and selectivity with a very high catalytic stability at 1073 K. The Pt/K (0.3 wt%)-Al₂O₃ catalyst showed a good performance but a slightly lower conversion level than Pt/Na (0.3 wt%)-Al₂O₃. On the other hand, the Pt/Al₂O₃ catalyst displayed an important decrease of the methane conversion through the reaction time at 1073 K and hence, a lower catalytic stability due mainly to the carbon deposition. It can be concluded that either Na or K addition to Pt/Al₂O₃ enhances the catalytic stability since they provide basic sites, which favour the dissociation reaction of CO₂ into CO and O. The O species can react with the carbon deposited on the Pt, thus cleaning the metallic phase of the doped catalysts.

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1. Introduction

The transformation of natural gas into syn-gas or more valuable products has acquired a special importance since the reserves of natural gas in the world are higher than the petroleum ones. Alternative processes such as steam reforming and partial oxidation of methane present several difficulties due to both the high operation and equipment costs. In consequence, the study of the methane reforming with CO₂ appears as an important alternative way to obtain syn-gas.

In spite of the initial difficulties, the study of the methane reforming with CO₂ has been progressively increased. A very important driving force to develop new technologies and catalysts is derived from the potential application of this process for the preservation of the environment, since CO₂ plays an important role in the greenhouse effect. In this sense, the development of this process could contribute to

the diminution of CO₂ emissions to levels close to those established in the Kyoto Protocol [1]. Furthermore, a comparative cost study about the production of acetic acid using three processes (steam reforming, partial oxidation and CH₄ reforming with CO₂) was reported in the literature and showed that the operative cost of the methane reforming with CO₂ is lower than those of the other two processes [2]. Hence, this process seems to be a promising route from an economic point of view and also appears to be an adequate tool for the environmental protection.

From the above comments, it can be inferred that it is necessary to develop new technologies for the capture and re-use of the blown CO₂. The use of CO₂ by means of proper technologies would contribute not only to the reduction of its emissions but also would introduce additional economic benefits derived from the aggregated value of the chemical products which can be obtained from CO₂. On this basis, important efforts are being done in order to develop new catalysts with high activity and selectivity and good stability in the syn-gas production by using methane reforming with CO₂ [3]. It is worth noticing that the methane reforming with

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CO₂ produces a syn-gas with a H₂/CO molar ratio close to 1, but this process has not industrial application yet [4].

The main challenge for the industrial application of the methane reforming with CO₂ is related to the development of active catalytic materials but with very low coke formation rate either on the catalysts or in the cold zones of the reactor. The carbon formation in this process can be controlled by using a support that favours the dissociation reaction of CO₂ into CO and O, the last species being the responsible for the cleaning of the metallic surface [5].

Results obtained by using supported Ni catalysts showed very high deactivation rates compared with catalysts based on noble metals [6]. Taking into account these findings, it can be inferred the promising behaviour of noble metals in this reaction [7,8]. In fact, Rostrup-Nielsen and Hansen [9] studied the behaviour of Ni, Ru, Rh, Pd, Ir and Pt supported on MgO in the reforming of methane with CO₂ process. They found that Ru/MgO and Rh/MgO exhibited both good activity and selectivity, and a very low coke deposition. Seshan et al. [10] tested several catalytic formulations containing Ni or Pt supported on γ -Al₂O₃ and ZrO₂, and they found that Pt/ZrO₂ was a very stable catalyst during the operation in contrast with Pt/Al₂O₃ and those based on Ni. Bitter et al. [8] studied the effect of the support (Al₂O₃, ZrO₂, TiO₂ and SiO₂) on Pt-based catalysts and they found that the use of an adequate support can also increase the activity of Pt. Besides, Tsipouriari et al. [11] using Rh deposited on TiO₂, γ -Al₂O₃, MgO, SiO₂, CeO₂ and ZrO₂ stabilized with Y₂O₃, observed a strong influence of the support on the specific activity and on its deactivation during the reaction.

It was reported in the literature that the behaviour of supported metallic catalysts in the methane reforming with CO₂ depends on several interrelated factors such as the nature of the metal, the support type, the metallic particle size and the characteristics of the metal–support interface [7,8,11–13].

Taking into account that there is no literature related to the use of alkali metal-doped alumina as a support of noble metals for the reaction of methane reforming with CO₂, this paper reports a study of the catalytic performance of Pt/Na-Al₂O₃ and Pt/K-Al₂O₃ catalysts with different alkali metal contents at different reaction temperatures (823–1073 K). Besides, the behavior of these catalysts was compared with that of Pt/Al₂O₃ and Pt/ZrO₂ in experiments at high temperature (1073 K) and long reaction times. Catalysts were characterized by test reaction of the metallic phase (cyclohexane dehydrogenation), temperature programmed reduction (TPR) and temperature programmed oxidation (TPO), in order to obtain a relationship between the structure of catalysts and the catalytic performance (activity, selectivity and stability).

2. Experimental

Four supports were used for the preparation of the metallic catalysts: (i) a commercial γ -Al₂O₃ (CK 300 from

Cyanamid Ketjen), (ii) γ -Al₂O₃ (CK 300) doped with two different Na amounts (0.3 and 1 wt%), (iii) γ -Al₂O₃ doped with 0.3 and 0.5 wt% K and (iv) ZrO₂ (0404 T from Engelhard). The doping of γ -Al₂O₃ (previously calcined at 1073 K) with Na and K was carried out by impregnation of the support with aqueous solutions of NaOH and KOH, respectively. The amounts of the alkali metals in the impregnating solutions were such as to obtain the desired loadings. After the deposition of the alkali metal, samples were dried at 393 K for 24 h and then calcined at 1073 K for 4 h. The metallic supported catalysts were prepared by impregnation of the supports with an aqueous solution of H₂PtCl₆. The impregnating volume/weight support ratio was 1.4 ml g⁻¹, and the concentration of Pt in the impregnating solution was such as to obtain the desired Pt loading (1 wt%). The impregnation time was 6 h, and then the samples were dried at 393 K for 24 h.

In order to study the influence of the thermal treatments on the surface area of ZrO₂, Al₂O₃ and the alkali metal-doped Al₂O₃, two different He treatments were carried out on these supports: one of them at 923 K and the other one at 1073 K, both during 8 h. The measurements of the surface area were performed in a Micromeritics ASAP 2000 with N₂ at 77 K.

The effect of the previous thermal treatments in flowing He (for 4 h) on the catalytic activity in cyclohexane dehydrogenation was studied at two temperatures of the He treatment: 923 and 1073 K. Cyclohexane dehydrogenation reaction was carried out in a differential flow reactor. Prior to the reaction, samples were reduced “in situ” with H₂ at 773 K. The H₂/hydrocarbon molar ratio was 26 and the reaction temperature was 573 K.

The different catalysts were tested in the methane reforming with CO₂. The reaction was carried out in a flow equipment. The samples (0.17 g) were first reduced under flowing H₂ at 823 K for 3 h. Then, the catalysts were heated under He up to the reaction temperature (between 823 and 1073 K). After the catalysts reached the reaction temperature, the CH₄/CO₂ mixture (CH₄/CO₂ molar ratio = 1) was fed to the reactor with a flowing rate of 20 ml min⁻¹. In order to avoid diffusional effects, catalyst particle sizes were very small (<80 mesh). The reaction time was 285 min. The reaction products were analyzed by using an on-line chromatographic system (GC–TCD) containing a Supelco Carboxen 1006 PLOT (30 m × 0.53 mm) column. In order to study the catalytic stability, additional experiments were performed during longer reaction times (5800 min) at 1073 K.

TPR measurements were carried out by using a H₂ (5% v/v)–N₂ reductive mixture with a heating rate of 6 K min⁻¹. The temperature was increased from room temperature up to 850 K. Prior to the experiments, samples were calcined in flowing air at 773 K for 3 h.

Temperature programmed oxidation measurements were carried out in an apparatus with an intermediate methanation device coupled with a flame ionization detector (FID).

The catalyst sample was heated from room temperature up to 923 K at 12 K min^{-1} in an oxidizing gas stream (30 ml min^{-1} , 2.3% O_2 in N_2) [14].

3. Results and discussion

Figs. 1–3 show the initial values (measured at 30 min of the reaction time) of the CH_4 conversion, CO_2 conversion and the H_2/CO molar ratio, respectively, as a function of the reaction temperature for the different catalysts. Fig. 1 displays that the CH_4 conversions are far from the equilibrium at low reaction temperatures. When the reaction temperature increases, the CH_4 conversions increase, and it should be noted that these values are close to the equilibrium ones, except for the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. A similar behaviour was also observed for CO_2 conversions (Fig. 2). The H_2/CO molar ratios at low reaction temperatures display some differences between the different catalysts (0.30 for Pt/K (0.5 wt%)- Al_2O_3 and 0.44 for Pt/Na (1 wt%)- Al_2O_3), but it is observed that when the reaction temperature increases, the H_2/CO molar ratios are similar for the different samples, reaching values between 0.6 ($\text{Pt}/\text{Al}_2\text{O}_3$) and 0.62–0.65 for the remaining samples at 1073 K. Taking into account the CH_4 and CO_2 conversions, and the H_2/CO molar ratio results, it can be observed a low effect on the catalytic behaviour when the Na or K loading increases. Furthermore, it appears that the addition of a low amount of Na or K (0.3 wt%) leads to slightly higher conversions than the addition of 1 wt% Na or 0.5 wt% K.

In order to study the catalytic stability, four samples were selected: Pt/Na (0.3 wt%)- Al_2O_3 , Pt/K (0.3 wt%)- Al_2O_3 ,

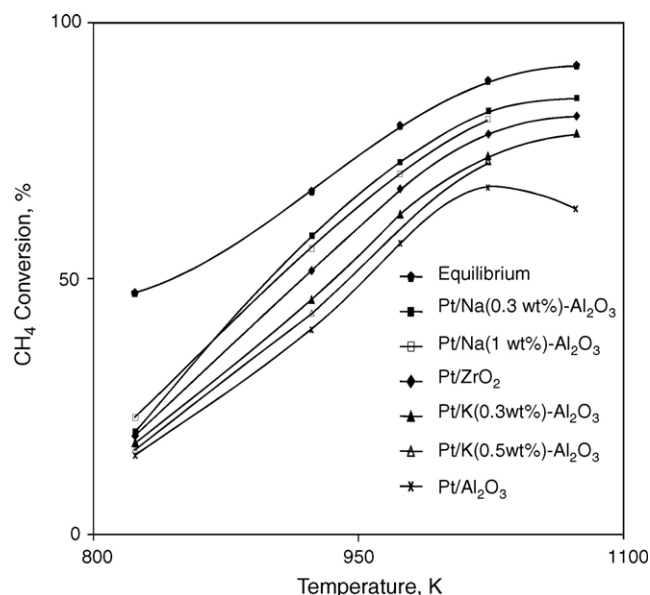


Fig. 1. CH_4 conversion for the different catalysts in the methane reforming with CO_2 as a function of the reaction temperature. Conversion values were measured at 30 min on stream. $\text{CH}_4/\text{CO}_2 = 1$. Residence time = 0.51 g s ml^{-1} .

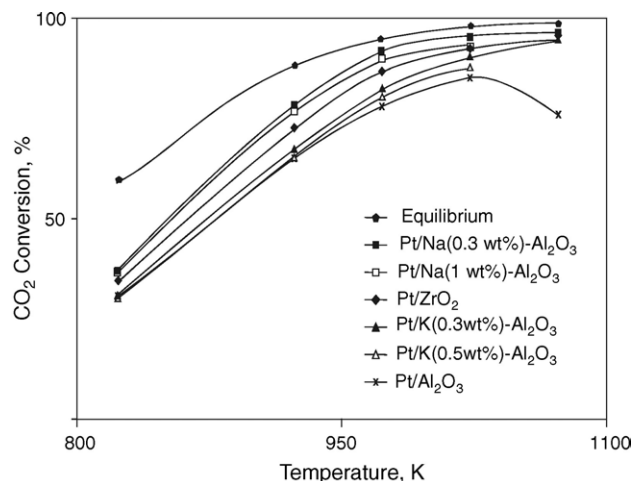


Fig. 2. CO_2 conversion for the different catalysts in the methane reforming with CO_2 as a function of the reaction temperature. Conversion values were measured at 30 min on stream. $\text{CH}_4/\text{CO}_2 = 1$. Residence time = 0.51 g s ml^{-1} .

Pt/ZrO_2 and $\text{Pt}/\text{Al}_2\text{O}_3$. These samples were tested at the same residence time as the above-mentioned experiments (0.51 g s ml^{-1}) and at 1073 K (where the highest conversions were obtained) for 5800 min of reaction time. Figs. 4–6 show the values of CH_4 and CO_2 conversions and the H_2/CO molar ratio as a function of the reaction time, respectively. It can be observed in Figs. 4 and 5 that the CH_4 and CO_2 conversions slightly decrease up to 285 min, and then they remain practically constant for Pt/Na (0.3 wt%)- Al_2O_3 , Pt/K (0.3 wt%)- Al_2O_3 and Pt/ZrO_2 catalysts. In the case of the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst, a continuous decrease in the CH_4 and CO_2 conversions is clearly observed through the reaction time. Moreover, the H_2/CO molar ratio (Fig. 6) is practically constant for Pt/Na (0.3 wt%)- Al_2O_3 , Pt/K (0.3 wt%)- Al_2O_3 and Pt/ZrO_2 catalysts, but it is

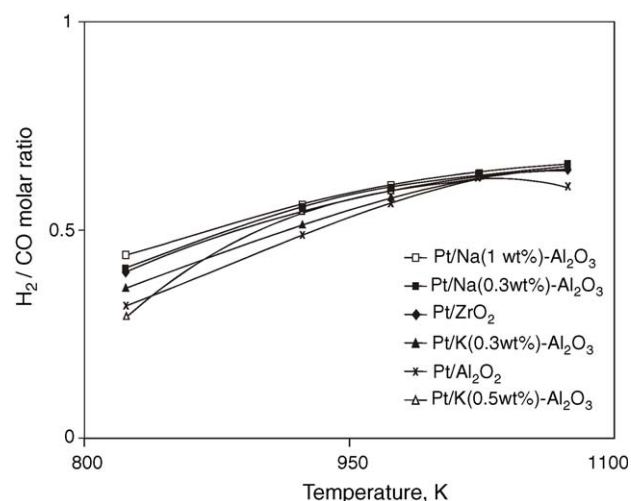


Fig. 3. H_2/CO molar ratio values for the different catalysts in the methane reforming with CO_2 as a function of the reaction temperature. Values were measured at 30 min on stream. $\text{CH}_4/\text{CO}_2 = 1$. Residence time = 0.51 g s ml^{-1} .

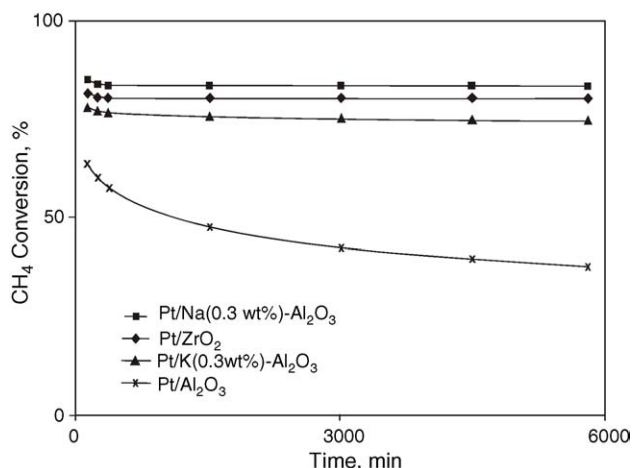


Fig. 4. CH₄ conversion for the different catalysts in the methane reforming with CO₂ at 1073 K as a function of the reaction time. CH₄/CO₂ = 1. Residence time = 0.51 g s ml⁻¹.

observed a continuous decrease of this molar ratio through the reaction time for the Pt/Al₂O₃ catalyst. From these results, it can be concluded that the stability of Pt/Na (0.3 wt%)-Al₂O₃, Pt/K (0.3 wt%)-Al₂O₃ and Pt/ZrO₂ catalysts is clearly higher than that of the Pt/Al₂O₃ one. Fig. 6 also shows that the H₂/CO molar ratio in the product stream is lower than one, even though the stoichiometry of the reforming reaction would indicate a theoretical H₂/CO molar ratio equal to one. This effect is associated with the reverse water–gas shift reaction (RWGS). This reaction consumes part of the H₂ produced by reforming, which reacts with CO₂ to yield CO and water. It can be also observed that this RWGS reaction is favoured over the Pt/Al₂O₃ catalyst, since the H₂/CO molar ratio obtained for this catalyst is lower than those obtained for the other samples. The same explanation can be applied to the results showed in Fig. 3. Besides, from results displayed in Figs. 4–6, it is worth noticing that the Pt/Na (0.3 wt%)-Al₂O₃ shows the better

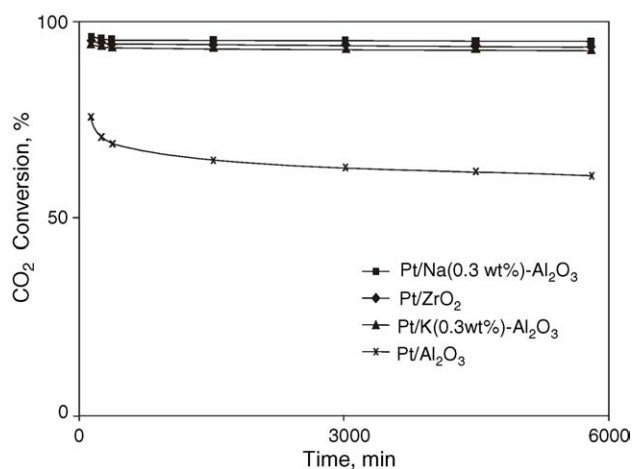


Fig. 5. CO₂ conversion for the different catalysts in the methane reforming with CO₂ at 1073 K as a function of the reaction time. CH₄/CO₂ = 1. Residence time = 0.51 g s ml⁻¹.

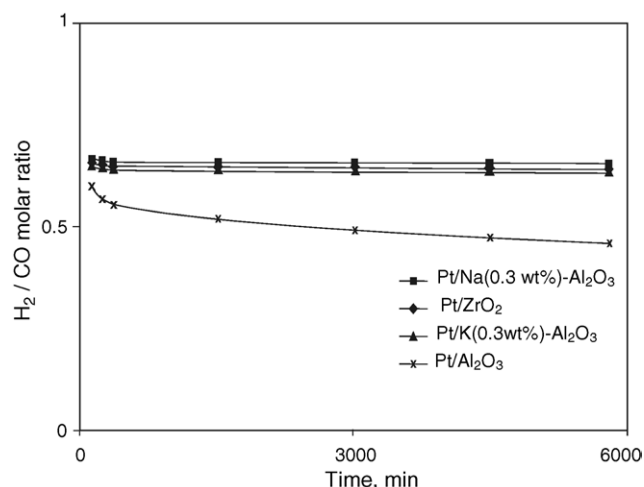


Fig. 6. H₂/CO molar ratio values for the different catalysts in the methane reforming with CO₂ at 1073 K as a function of the reaction time. CH₄/CO₂ = 1. Residence time = 0.51 g s ml⁻¹.

catalytic performance, while the Pt/Al₂O₃ catalyst displays the lowest CH₄ and CO₂ conversions, and the lowest H₂/CO molar ratios through the reaction time.

In order to study the thermal stability of the supports, additional experiments were carried out. Thus, the different supports (Al₂O₃, ZrO₂, Na and K-doped alumina) were treated under flowing He at two temperatures (923 and 1073 K) for 8 h, and then the specific surface area were determined. Table 1 shows the effect of the thermal treatment on the surface area of the different supports. It can be observed that Al₂O₃ shows a very slow decrease in the specific surface area after the He-treatment between 923 and 1073 K. If Na or K are added to Al₂O₃, a higher decrease in the surface area is observed (about 20%) when the temperature of the He-treatment increases. In the case of ZrO₂, it shows a decrease of about 30% in *S*_{BET}.

Fig. 7 shows the initial cyclohexane dehydrogenation rates (*r*_{ch}) of the different fresh monometallic catalysts prepared on the different supports calcined at 1073 K in order to study the thermal stability of the metallic phase. These catalysts were submitted to a thermal treatment under flowing He at two temperatures: 923 and 1073 K for 4 h. After this treatment, the samples were reduced under flowing H₂ at 773 K, and then the test reaction (cyclohexane dehydrogenation) was carried out at 573 K. It should be

Table 1
Specific surface area (*S*_{BET}) of the supports after treatment with flowing He at 923 and 1073 K

Support	<i>T</i> (K)	<i>S</i> _{BET} (m ² g ⁻¹)
ZrO ₂	923	27.5
ZrO ₂	1073	21.5
Al ₂ O ₃	923	180
Al ₂ O ₃	1073	176
Na (0.3 wt%)-Al ₂ O ₃	923	180
Na (0.3 wt%)-Al ₂ O ₃	1073	146
K (0.3 wt%)-Al ₂ O ₃	923	180
K (0.3 wt%)-Al ₂ O ₃	1073	149

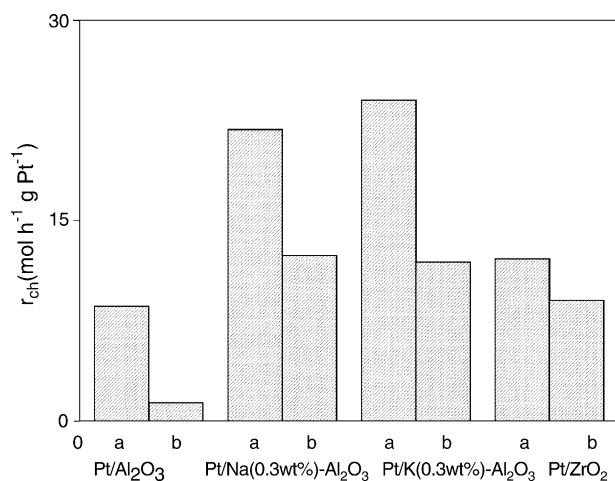


Fig. 7. Initial reaction rates (r_{ch}) in cyclohexane dehydrogenation for different catalysts. Reaction temperature: 573 K. Samples pretreated in He at: (a) 923 K for 4 h and (b) 1073 K for 4 h.

indicated that the cyclohexane dehydrogenation is an insensitive-structure reaction [15] and, in consequence, this reaction can be considered as an indirect measurement of the Pt dispersion. It can be observed that the Pt/Al₂O₃ catalyst shows a very important decrease in the cyclohexane dehydrogenation activity (about seven times) when the temperature of He-treatment increases from 923 up to 1073 K. In the case of the fresh Pt/Na (0.3 wt%)-Al₂O₃ catalyst, the cyclohexane activity decreases 42% between 923 and 1073 K, and for the fresh Pt/K (0.3 wt%)-Al₂O₃, the cyclohexane dehydrogenation capacity decreases 50%. In the case of the fresh catalysts based on ZrO₂, the initial cyclohexane dehydrogenation rate is affected in a low extension when the temperature increases from 923 up to 1073 K. These results would indicate that fresh Pt/ZrO₂, Pt/Na-Al₂O₃ and Pt/K-Al₂O₃ catalysts showed a higher thermal stability of the metallic phase than the Pt/Al₂O₃ one. Besides, it can be inferred from these results that the metal dispersion and its stability strongly depend on the nature of the supports. In this sense, Bitter et al. [8] also found a very important effect of the support type on the Pt dispersion.

Fig. 8 shows the TPO profiles of the different samples after reaction time of 5800 min at 1073 K. It can be observed that the Pt/Al₂O₃ displays a defined TPO profile. On the other hand, the used Pt/ZrO₂, Pt/Na-Al₂O₃ and Pt/K-Al₂O₃ catalysts show very weak signals during the TPO experiments, which indicate a negligible carbon deposition. Hence, only the Pt/Al₂O₃ sample shows a certain amount of the deposited carbon (lower than 0.2 wt%) after 5800 min of the reaction time. The carbon deposition on this sample could be responsible for the important decay in the CH₄ and CO₂ conversions through the reaction time (such as Figs. 4 and 5 show). Likewise, the H₂/CO molar ratio is also decreased by the accumulation of carbon in the Pt/Al₂O₃ catalyst. One probable explanation is that the carbon deposition from CH₄ dissociation on both the metallic and acidic centers of the support is faster than the dissociation of

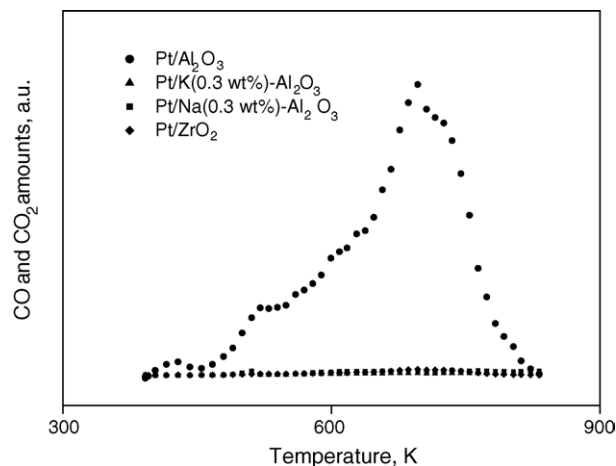


Fig. 8. CO₂ and CO production during the TPO experiments carried out on different catalysts.

CO₂ into CO + O in the interface between the metal particles and the support. It must be remembered that the O species produced in the interface could partially eliminate the carbon deposited on the metal. The accumulation of the carbon leads to an important blocking of the metallic surface and in consequence the H₂ formation progressively decreases, thus justifying the decrease of H₂/CO molar ratio through the reaction time. This explanation is in agreement with what Nagaoka et al. [16] reported. However, the participation of the RWGS reaction should also be taken into account in order to explain the evolution of the H₂/CO ratio through the reaction time.

In the case of Pt/Na-Al₂O₃ and Pt/K-Al₂O₃ catalysts, the addition of alkali metal ions to Al₂O₃ not only inhibits the acidic sites of the support [17] but also increases the basic character of the catalysts [18]. In this sense, the presence of the basic sites in the metal-support interface favours the CO₂ adsorption and the subsequent CO₂ dissociation rate into CO and O species [19]. The last species could react with the carbonaceous residues placed on the metallic phase, thus cleaning its surface. Hence, a higher stability for these catalytic systems can be expected. In the case of Pt/ZrO₂, a similar behaviour was reported in the literature [16].

In order to study with more detail the possible modification of the structure of the different catalysts, additional TPR experiments were carried out on samples after 285 and 5800 min of reaction time at 1073 K. The samples were withdrawn from the reactor and submitted to an oxidation treatment in air at 773 K during 3 h before the TPR measurements. It can be observed in Fig. 9 that the TPR profiles of the used catalysts after 285 min of reaction time are different according to the type of support used for the preparation. It should be noted that the TPR profiles of Pt/Al₂O₃ and Pt/ZrO₂ samples display very small differences when the reaction time increases from 285 min up to 5800 min. These findings are in agreement with the results reported by Nagaoka et al. [16]. Taking into account the

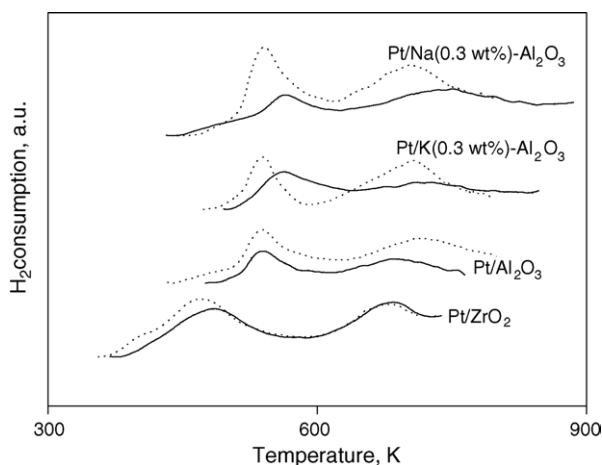


Fig. 9. TPR profiles of different catalysts after reaction at 1073 K for 285 min (—) and 5800 min (---) of reaction time. Samples were calcined at 773 K before the TPR measurements.

results on Pt/Al₂O₃, it can be concluded that the lower stability of this catalyst is mainly due to the carbon deposition, since the structure of the metallic phase is slightly affected through the reaction time. On the contrary, TPR profiles of catalysts based on Na and K-doped Al₂O₃ show important differences when the reaction time is increased. These modifications could be due to two probable effects: (i) the change in the distribution of the metallic particle sizes and (ii) the formation of different intermetallic species. However, these modifications do not appear to be relevant in the activity, selectivity and stability of these catalytic systems according to the results shown in Figs. 4–6. These results indicate a certain insensitive structure character of this reaction for Pt/Na-Al₂O₃ and Pt/K-Al₂O₃ catalysts. In the case of the Pt/ZrO₂ catalyst, a negligible modification of its metallic structure through the reaction time is observed. This fact and the very small carbon deposition detected by TPO can explain the excellent catalytic stability of this sample.

4. Conclusions

The Pt/Na-Al₂O₃ catalyst displays a higher catalytic performance than Pt/K-Al₂O₃ and Pt/ZrO₂ ones, with a good catalytic stability after 5800 min of the reaction time in the methane reforming with CO₂ at 1073 K. These catalysts do not show any carbon deposition through the reaction time. On the contrary Pt/Al₂O₃ showed a poor performance in this reaction and a low stability, which can be caused mainly by

the carbon formation, such as it was determined in the TPO experiments. It should be also indicated that the metallic structure of the Pt/Al₂O₃ catalyst showed a small modification through the reaction time, in a similar way as the Pt/ZrO₂ sample. In the case of Pt/Na-Al₂O₃ and Pt/K-Al₂O₃ catalysts, a certain modification of the structure of the catalysts through the reaction time was found, probably due to changes in the metallic particle size distribution or the formation of new intermetallic species. However, these structural effects do not appear to have an incidence on the catalytic stability.

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