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# High throughput experimentation applied to the combustion of methane and a comparison with conventional micro-reactor measurements

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## Abstract

High throughput experimentation (HTE) was performed in order to investigate the behavior of various supported palladium catalysts during the catalytic combustion of methane. Results indicate that both titania- and tin-supported catalysts show the highest activity for this reaction. The activity of some of the catalysts analyzed is affected by a reducing pretreatment and, contrarily to widespread opinion, it is shown that $CO_2$ is not inert towards the reaction process and can even have an activating effect on the catalyst, depending on the kind of support used. An acceptable correlation is found between the results obtained in catalytic tests performed in HTE and those obtained in a conventional laboratory micro-reactor. However, HTE results must be interpreted in a qualitative rather than in a quantitative way. Characterization results of catalysts used in both techniques are the same.

*Keywords:* Methane; Catalytic combustion; Palladium; Support; Combinatorial; Carbon dioxide

## 1. Introduction

The catalytic combustion (CC) of methane is a promising way for the production of energy at higher yields, lower costs and lower pollutants emissions levels [1–3]. To improve this technology, attention has to focus towards a comprehensive understanding of the reaction mechanisms and, in particular, towards the dynamic phenomena occurring at the surface of the catalyst at work. The investigation of new catalytic systems is also necessary with the hope to find a more active and/or stable system and to discover new phenomena. The most adequate way to get rapid and complete information on these aspects is probably to use high throughput experimentation (HTE) and combinatorial analysis techniques. The main objective of this work is to apply this approach to the study of some catalysts used in the low temperature range combustion of $CH_4$ in order to get information to: (i) improve the catalyst efficiency and (ii) detect new phenomena occurring during the reaction. In this work, catalysts were prepared in a conventional way, i.e., without the participation of “multiple serial preparation methods” (as with automatic robots), and the catalytic performances were measured in a matrix containing small parallel reactors. The application of HTE is criticized because the conditions under which HTE is performed are not representative of conditions used in conventional laboratory micro-reactor (MR) tests [4]. The criticism is mainly based on the lack of characterization of the catalysts used in HTE. Therefore, in order to get some light on these aspects, some catalysts tested both in HTE and in MR experiments, were characterized by BET, XRD and XPS and the results were compared. A first attempt to correlate the catalytic activity measured by both techniques is also performed. Concerning the CC of methane, literature results show that the nature of the support, the treatment of samples before reaction and the reaction products, in particular $CO_2$, are important variables that affect the catalytic performances [5]. In this paper, these aspects are studied and discussed.

## 2. Materials and methods

### 2.1. Samples preparation

(i) *Pd/alumina catalyst.* 2 wt.% Pd/$\gamma$-$Al_2O_3$ was prepared by the incipient wetness technique as described in [6]. It

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was reduced by a gaseous treatment during 3 h at 673 K under $H_2$ 5%/$N_2$ and calcined 3 h at 873 K under air.

(ii) *Pd-catalysts using other supports*. The same procedure was followed but using different supports: titania, zirconia, tin oxide, ceria–zirconia and alumina–silica.

### 2.2. Catalytic activity measurements

(i) *HTE experiments*. The tests were performed in a multichannel parallel reactor (COMBI Reactor$^{TM}$) containing 10 reactors, described in detail elsewhere [7]. The space velocity in each well (4 mm i.d.) was set to $18.75 \times 10^{-2}$ $m^3\,g^{-1}\,h^{-1}$ and kept constant in all experiments. Each channel was fed with a gaseous mixture composed of $CH_4/O_2/He = 1/5/94$ vol., except for the experiments carried out in the presence of 5% $CO_2$ ($CH_4/O_2/CO_2/He = 1/5/5/89$ vol.), at a flow rate of 50 ml/min. The amount of catalyst used in each channel was 100 mg (particle size between 100 and 315 μm) and the reaction was run between 473 and 773 K.

(ii) *MR experiments*. Tests were performed in a conventional fixed-bed micro-reactor (8 mm i.d.). The operating conditions were close to those used in the HTE experiments. The space velocity was the same as in HTE. The amount of catalyst was 320 mg (particle size between 100 and 315 μm) and the reaction was run between 473 and 823 K. Two kinds of tests were performed: (i) in the absence of 3% $CO_2$ ($CH_4/O_2/He = 1/10/89$ vol.) and (ii) in the presence of $CO_2$ in the gaseous reactants feed ($CH_4/O_2/CO_2/He = 1/10/3/86$ vol.).

In both HTE and MR experiments, the activity of the catalyst was measured every 50 K in a stepwise way with a staying time of 1 h at each temperature. The methane conversion curves were plotted as a function of the temperature and the $T_{50}$ values, which are the temperatures necessary to reach 50% of methane conversion, were obtained by interpolation.

### 2.3. Characterization

XRD, BET and XPS were used. The characterization methods are described in detail in [6]. Some DRIFTS experiments were also performed.

## 3. Results and discussion

### 3.1. HTE experiments

#### 3.1.1. Influence of a reducing pretreatment

Catalysts were tested both (i) after an in situ reducing pretreatment ($H_2$ 40%/He, 50 ml/min, at 573 K overnight) and (ii) without any pretreatment (untreated catalysts).

*3.1.1.1. Catalysts after in situ reducing pretreatment.* The results displayed in Fig. 1 indicate that the most active catalysts are those based on tin or titanium oxides (90 and 88% conversion at 773 K, respectively, versus 66% for the Pd/γ-$Al_2O_3$). At lower temperature, the titania-based catalyst is much more active than the tin-supported catalyst: at 623 K, the $CH_4$ conversion values are 48 and 14%, respectively, and de difference between the temperatures necessary to get 50% of conversion, for each catalyst ($\Delta T_{50}$) is as large as 60 K. An important fact is that Pd/γ-$Al_2O_3$ is not the most active catalyst. These results are quite important because, even though tin oxide has already been reported as a good support for the palladium-based catalysts for the CC of $CH_4$ [8], alumina is the most used and studied support for this reaction [3]. The alumina–silica support is fairly good (56% at 773 K), giving rise to an activity which is a little bit

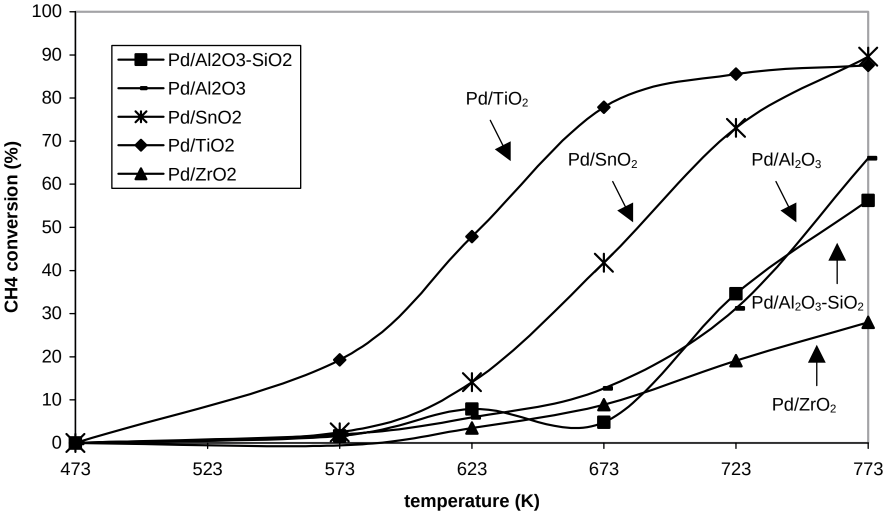

Fig. 1. Conversion of methane as a function of the temperature for various supported palladium 2 wt.% catalysts, after a reducing pretreatment (under $H_2$ 40% at 573 K overnight).

lower than that of the γ-alumina-supported catalyst. Zirconia seems to be a very poor support for the reaction, at least in this temperature range. This result might be surprising due to the common use of such a material for gas turbine applications, given its ability to increase both the stability and the activity of the catalyst at high temperature. However, one should notice that the activity tests reported in this work were performed at low temperature (below 773 K) and are probably only valid for this temperature range. These results must be checked at higher temperature to get more conclusive trends on this kind of material. It is important to mention that the poor activity of Pd/zirconia catalysts can also be due to the choice of the palladium precursor (a chlorinated one) since XPS analysis revealed higher concentrations of Cl on that catalyst if compared with the other supports (almost 10% versus less than 0.5% for the other materials). Thus, the use of a chlorinated palladium precursor is likely to have a detrimental effect on the activity of zirconia-supported catalysts. The influence of the palladium dispersion might also be invoked in order to explain the obtained results, but the CO-chemisorption technique could not be applied on this material (zirconia) given its CO adsorptive character.

No characterization results are available for these catalysts after the in situ reducing pretreatment, but they were analyzed after the reaction. Results indicate that, if compared with fresh catalysts, no significant changes could be identified either by XRD or by XPS. These results tend to demonstrate that, even if it was pre-reduced, the catalyst is reoxidized under reaction conditions and its behavior progressively approaches that of an oxidized material.

*3.1.1.2. Catalysts without pretreatment (untreated).* Activity measurements were performed on fresh, untreated catalysts, i.e. in an oxidized form (Fig. 2). The results clearly show that, under these conditions, both the titania- and the tin-based catalysts remain the best ones, but the activity gap between them dramatically decreases ($\Delta T_{50} = 10\,\text{K}$ versus 60 K), if compared with the situation observed after an in situ reducing pretreatment. This indicates that the reducing pretreatment is important to improve the catalytic activity but its effect and its extent depend on the kind of catalyst support. However, whether a reducing pretreatment is applied or not, both the titania- and the tin-based catalysts are the best ones, followed by the alumina-supported catalyst. The zirconia-based catalyst is once again the poorest material (13% of $CH_4$ conversion at 773 K). However, a reducing pretreatment renders it much more active than the untreated catalyst (28% at 773 K). The same observation can be made on the titania material, which is also much more active ($T_{50} = 628\,\text{K}$ versus 668 K) after a reducing pretreatment. The influence of a reducing pretreatment is quite different on the tin-, the alumina- and the alumina–silica-based catalysts. Indeed, they show the same activity, were they reduced or not. Then, it could be suggested that the influence of the reduction pretreatment would be related to the reducibility of the support given that $TiO_2$ and $ZrO_2$ are reducible oxides [9], which is not the case for the other supports. These results tend to suggest that a reducing treatment has an activating effect principally on reducible supports like $TiO_2$ and $ZrO_2$. It is not excluded that this activating effect could also be related either to the development of some interaction between the palladium and the support material or to some migration of some active reducing species (spillover process).

### *3.1.2. Influence of the presence of a reaction product ($CO_2$)*

The response of some of these untreated catalytic systems towards the presence of 5% of $CO_2$ was highly dependent on the support (Table 1). On alumina, the activity was strongly inhibited by the presence of $CO_2$ ($T_{50} = 773\,\text{K}$ versus 758 K) whereas on ceria–zirconia mixed oxides-based catalysts, the activity significantly increased in the presence

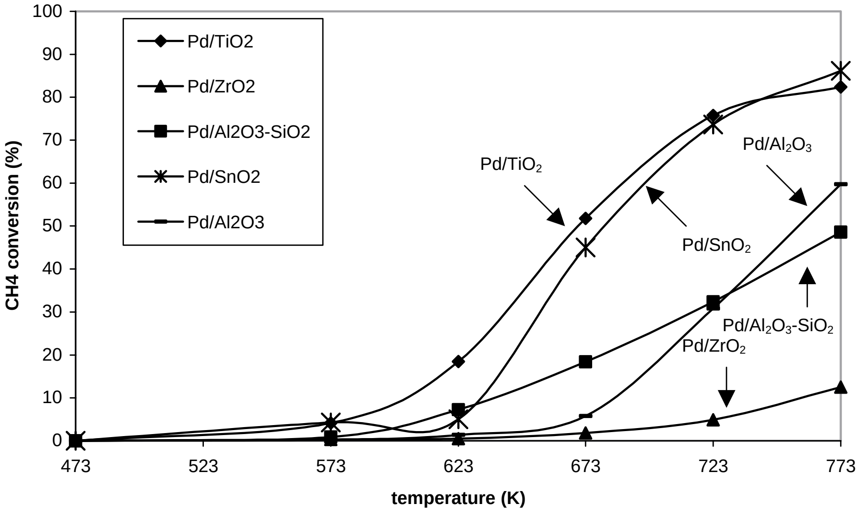

Fig. 2. Conversion of methane as a function of the temperature for various supported palladium 2 wt.% catalysts, without any pretreatment.

Table 1
Comparison of the temperature necessary to get 50% of $CH_4$ conversion ($T_{50}$), obtained on different catalytic systems with (+) and without (−) the addition of $CO_2$ into the reactants feed, both in HTE and in MR tests

| Catalyst | $CO_2$ | $T_{50}$ (K) | |
|---|---|---|---|
| | | HTE | MR |
| $PdO/TiO_2$ | − | 668 | 638 |
| $PdO/TiO_2$ | + | 673 | 643 |
| $PdO/SnO_2$ | − | 678 | 663 |
| $PdO/SnO_2$ | + | 683 | 673 |
| $PdO/Al_2O_3$ | − | 758 | 683 |
| $PdO/Al_2O_3$ | + | 773 | 703 |
| $PdO/Ce_{0.37}Zr_{0.63}O_2$ | − | ** | 818 |
| $PdO/Ce_{0.37}Zr_{0.63}O_2$ | + | 753 | 808 |

**: $T_{50}$ was impossible to be reached under those conditions.

of $CO_2$. Indeed, it was observed that the addition of some $CO_2$ into the feed allowed the catalyst to reach 50% of $CH_4$ conversion below 773 K. Such a conversion level was impossible to be reached in absence of $CO_2$ in the gaseous mixture. Thus, in this latter case, no $T_{50}$ values are available (indicated by the '**' symbol in Table 1). However, in order to assess the activating effect of $CO_2$ on this kind of catalyst, $CH_4$ conversion values obtained at 773 K (maximum temperature of experiment) both with and without the presence of $CO_2$ in the feed can be compared (61 versus 48% $CH_4$ conversion, respectively). Obviously, the presence of $CO_2$ induces an activating effect on the ceria–zirconia mixed oxides-based catalyst. Concerning both the titania ($T_{50} = 673$ K versus 668 K) and the tin-based catalysts ($T_{50} = 683$ K versus 678 K), the presence of $CO_2$ does not seem to significantly influence their activity, even though a slight inhibition can be suggested, considering the $T_{50}$ values. However, one should notice that the variations observed are tiny (±5 K) and might fall in the error range. These are new results, strongly indicating that the influence of $CO_2$ depends on the nature of the support. Characterization results (Table 2) indicate that this influence can neither be related to the surface area of the catalyst nor to any modification of the "Pd/metallic component of the support" XPS ratio. An attempt to explain the promoting effect of $CO_2$ observed on the $Pd/Ce_{0.37}Zr_{0.63}O_2$ catalyst comes from XPS results. The O 1s peak could be decomposed into two distinct O 1s species. The first O 1s species (low BE) is centered at around 529.5 eV and would be bound to Ce atoms whereas the other one (high BE) is located above 530.5 eV and is probably linked to other atoms like C or Zr. After reaction in the presence of $CO_2$, enrichment in low BE O 1s species was observed suggesting that, on Pd/Ce–Zr–O samples, some oxygen species might be formed in the presence of $CO_2$ [10]. These oxygen species would come from the dissociative adsorption of $CO_2$ on the surface, as it has been previously largely discussed [11]. It is suggested that this oxygen species could help to keep catalysts in a more oxidized state, improving the catalytic activity [6]. However, this is a tentative explanation which has to be confirmed on this kind of catalysts. In situ DRIFTS experiments performed under reaction conditions on Pd/alumina, in the presence of some $CO_2$, evidenced adsorption of carbonate species above 573 K. This is likely to explain the inhibiting effect of $CO_2$ observed on this kind of catalyst.

### 3.2. Comparison of characterization and catalytic activity results observed in both HTE and MR experiments

Interesting is the fact that characterization results obtained on catalysts after HTE and MR tests show a very good agreement as illustrated by XPS results, a very sensitive surface technique, expressed in terms of ratio of palladium on metallic component of the support (Table 2). Obviously, atomic ratios are similar for catalysts used in HTE and MR. Binding energies were identical, too. This evidences the fact that the surface state of the catalysts using both techniques is the same. XRD results were also identical.

A first attempt to compare activity results obtained in both HTE and MR is proposed and discussed here, based on the $T_{50}$ values furnished by each technique. When comparing the $T_{50}$ values obtained by HTE and MR methods (Table 1), a good agreement is observed. The inhibiting effect due to the presence of $CO_2$ could be identified in both kinds of tests on the alumina-supported catalyst ($\Delta T_{50} = +20$ K in MR versus +15 K in HTE), while on both the tin- and the titania-based catalysts, a slight inhibition was found due to the presence of $CO_2$ ($\Delta T_{50} = +10$ K versus +5 K and +5 K versus +5 K, respectively). On palladium supported on ceria–zirconia mixed oxide catalyst, the activity increased in the presence of $CO_2$, in both cases ($T_{50} = 808$ K versus 818 K in MR, see previous discussion for HTE). Thus, it

Table 2
Experiments both with (+) and without (−) the addition of some $CO_2$ into the gaseous feed

| | BET SA[a] ($m^2 g^{-1}$) | HTE[b] ($\times 10^{-4}$) | | MR[b] ($\times 10^{-4}$) | |
|---|---|---|---|---|---|
| | | Without $CO_2$ | With $CO_2$ | Without $CO_2$ | With $CO_2$ |
| $PdO/TiO_2$ | 43 | 287 | 269 | 300 | 313 |
| $PdO/SnO_2$ | 8 | 461 | 415 | 435 | 442 |
| $PdO/Al_2O_3$ | 61 | 80 | 85 | 83 | 76 |
| $PdO/Ce_{0.37}Zr_{0.63}O_2$ | 44 | 277 | 309 | 212 | 213 |

[a] Surface area of the fresh catalysts.

[b] XPS atomic ratios between palladium and the metallic component of the support after HTE and MR tests.

appears that the activity tendencies of the various studied catalysts towards the presence of $CO_2$ in the gaseous feed are well reproducible by the two techniques. This validates the use of HTE in order to evaluate and compare different catalysts in various conditions. Indeed, looking at the $T_{50}$ values obtained without the addition of $CO_2$ into the feed, the following activity order can be established in both HTE and MR techniques: $Pd/TiO_2 < Pd/SnO_2 < Pd/Al_2O_3 < Pd/Ce_{0.37}Zr_{0.63}O_2$. However, this ranking is no longer identical in both techniques, in the presence of $CO_2$, since HTE results indicate that $Pd/Ce_{0.37}Zr_{0.63}O_2$ is more active than $Pd/Al_2O_3$. Thus, activity tendencies of the various catalysts are rather well reproducible but discrepancies may exist and one should always keep it in mind. It is important to note that, despite the fairly good agreement between the two methods, the $CH_4$ conversion values in HTE are always lower, except for the $Pd/Ce_{0.37}Zr_{0.63}O_2$ catalyst, than those observed in MR tests. These quantitative differences can probably be related to inhomogeneities in the catalytic bed and/or heat effects in the reactors of the HTE system or, maybe, to the higher oxygen concentration used in MR experiments. Indeed, combustion is largely exothermic and heat transfer can have an important influence. Thus, as a general conclusion, the HTE method is an efficient tool to obtain the main activity trends of a catalytic library and identify the most promising samples for the studied reaction. It implies that HTE results must be interpreted in a qualitative rather than in a quantitative way. Therefore, after this first step has been completed, it is necessary to perform a more detailed analysis of the best catalysts by a conventional MR method, as has been previously proposed (selective combinatorial catalysis) [7].

## 4. Conclusions

1. The effective influence of a pretreatment of the catalyst actually depends on the kind of support used.
2. $TiO_2$ or $SnO_2$ seem to be interesting supports for the palladium active phase. Catalytic performances using these supports are higher when compared with alumina.
3. $CO_2$ in the feed could play an important role by increasing or inhibiting the catalytic performances. The exact role of $CO_2$ depends on the type of the support.
4. Characterization results of catalysts used in HTE and MR are similar; in particular, the surface state of catalysts after reaction is the same in both systems (XPS results).
5. Catalytic activity results obtained with HTE and MR show a good agreement. Activity tendencies are reproducible in both techniques.

The results of this work validate the approach of using HTE methods to accelerate the study of catalytic systems and to discover new phenomena. However, further verification of the most striking results in traditional systems is necessary for a complete understanding of the system under investigation.

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