Kinetic Analysis of Pd-based Methane Combustion Catalysts

F. Conti, A. Rossati, L.D. Vella, S. Specchia, V. Specchia

Dip. di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Torino – ITALY

1. General aspects

In recent years, catalytic combustion of CH₄ has been extensively studied as an alternative option to conventional thermal combustion [1,2] for the production of heat and energy in view of its capability to achieve effective combustion at much lower temperatures than in conventional oxidation processes. The catalytic combustion has shown to be highly efficient in gas turbine combustors [3,4] and effective in reducing the emitted pollutants such as CO and NOₓ [5-7]. CH₄ burners can operate under lean conditions so that the fuel efficiency can be much increased compared to stoichiometric conditions. Under lean-burn conditions, NOₓ emissions are much reduced; this is due to the cooler combustion resulting from the high air to fuel ratios at which the lean burners operate [3,4].

In view of its high activity, supported PdO is usually the employed catalyst for CH₄ combustion in applications which require low auto-ignition temperatures, such as in the treatment of CNG engine exhausts, and in catalytic combustors for gas turbines with ultra-low emissions [3]. Although several studies are reported in the literature on CH₄ combustion kinetics over Pd catalysts [8-15], there is no unanimity about the mechanisms of this reaction: Langmuir Hinshelwood [8-10], Eley-Rideal [11,12] and Mars van Krevelen [10,13-15] mechanisms have been proposed.

In this paper a kinetic study on two Pd-carried catalysts is presented: 2% Pd over NiCrO₄ and CeO₂·2ZrO₂. These two catalysts were previously studied for CH₄/air and CH₄/H₂/air lean mixtures oxidation in severe conditions in terms of temperatures and combustion space [16,17]. The catalytic combustion of CH₄, H₂ or other gaseous HC in a very small space, like a micro-burner, can represent, in fact, due to its easy controllability, an alternative method to produce contemporarily thermal and electrical energy [17].

2. Experimental

2.1. Catalysts preparation and basic characterization

In the present work, Pd/CeO₂·2ZrO₂ and Pd/NiCrO₄ catalysts were prepared by solution combustion synthesis (SCS). SCS is becoming one of the most important ways to produce a wide range of advanced porous ceramic or metallic materials, like nanostructured catalysts. SCS processes are in fact characterized by medium synthesis temperature (350-600 °C), fast heating rates and short reaction times, with the advantages of: i. formation of high purity products with a variety of size and shape, tunable with the synthesis conditions; ii. use of simple equipment; iii. cheap process compared to other conventional synthesis routes [5]. A homogeneous aqueous solution of metal nitrates as oxidizers (from Aldrich, 99% purity), and glycine (in case of CeO₂·2ZrO₂) or urea (in case of NiCrO₄) as fuel, dosed in stoichiometric ratio, once dissolved in distilled water, was placed into an oven at a selected temperature, around 600 °C [5,15]. Pd(NO₃)₂ was directly added to the precursors solution to co-synthesize 2% b.w. of Pd on the supports. Once placed in oven, the solution quickly began to boil, and the ignition of the glycine or urea took place. The as-prepared catalysts were the calcined in calm air for 2 h at 750 °C and then characterized: by XRD analysis (Philips X’PERT; Cu K
radiation), to assess the presence and purity of the expected phases and to gather information about their degree of crystallization; by BET specific surface area measurements (Micromeritics ASAP 2010 M apparatus, employing N₂ and degassing the samples in vacuum for at least 4 h at 250°C before analysis); by SEM-EDS analysis (SEM-EDS, LEO Supra 35), to assess the powder morphology.

The catalytic activity of the prepared catalysts towards CH₄ combustion was tested in a Temperature Programmed Oxidation (TPO) device. The apparatus consisted of a fixed bed reactor inserted between quartz wool (i.d. = 4 mm). The fixed bed was made of 0.05 grams of the selected catalyst (pressed in a pellet, crushed and sieved in the range 0.4-0.6 mm) and 0.95 of SiO₂ pellets (0.3-0.7 mm in size, from Unaxis). The SiO₂ pellets were used to increase the internal spacing between the catalyst powders and to reduce the pressure drop across the fixed bed. The latter was held in place between two layers of quartz wool.

The reactor was placed in a PID-regulated oven and a K-type thermocouple was inserted in the packed bed. The reactor was fed with 50 Nml min⁻¹ of gas (2.5% CH₄; 7.5%, O₂; He to balance). The temperature was increased from room to 850 °C with a slope of 50 °C min⁻¹ until the CH₄ combustion was ceased. When this condition was reached, the oven was allowed to cool by natural convection. During the oven cooling, the CH₄ concentration was measured every 10 °C. The reactor outlet gas concentration was monitored with a NDIR analyzer (Hartman and Braun URAS 10E) and recorded versus time by a computer. Sigma-shaped curves were obtained when plotting CH₄ conversion versus temperature and the half-conversion temperature (T₅₀) was regarded as an index of the catalytic activity.

### 2.2. Kinetics measurements

On the as-prepared catalysts, a reaction kinetics study was performed in order to establish the more appropriate kinetics law and the temperature dependence of the characteristic kinetic parameters. Fig. 1 shows a scheme of the experimental apparatus used for this purpose. The plant is based on a continuous recycle microreactor, employing the above described quartz tube for catalyst housing. The amount of pelletized catalyst is 0.5 g, diluted with 0.45 g of SiO₂. Recycle is enabled by a Teflon-membrane pump (KNF Italia). Analysis of the inlet and outlet gas feeds were performed via the above described analytical tools. The feed flow rate was kept equal to 50 Nml min⁻¹, whereas the overall recycle flow rate passing through the reactor was 1,050 Nml min⁻¹.

![Fig. 1 The lay out of the differential reactor.](image-url)

This was sufficient to eliminate almost any external mass transfer effect on the overall conversion measured. In such conditions, the maximum CH₄ concentration variation...
throughout the catalyst packed-bed was about 10%, as could be calculated on the basis of simple mass balances. Within these limits the average values of O₂ and CH₄ partial pressure in the catalyst were assumed as reference data for the assessment of a kinetic law. Besides, assuming a tortuosity factor equal to 2 for the catalyst pellets, it could be easily verified that also internal mass transfer was not significantly affecting the attained conversion (the catalyst effectiveness factor was always higher than 0.999). Runs have been performed in the temperature range 380-580 °C, whereas the absolute operating pressure was practically equal to 1 bar. The O₂ and CH₄ feed concentrations were varied in the ranges 2-15% and 0.5-2.5%, respectively, He being the balance.

3. Results and discussion

3.1. Catalysts basic characterization

The XRD diffraction patterns of the as-prepared catalytic powders showed that both the catalysts obtained by SCS presented a good crystalline degree, with very well detectable peaks of each components. In particular, Pd/CeO₂-2ZrO₂ appeared more crystallized than Pd/NiCrO₄. Moreover, no diffraction peaks related to Pd were detected, a sign that Pd dispersion was satisfactory. The BET values of the catalysts were 74.6 m² g⁻¹ for Pd/CeO₂-2ZrO₂ and 64.6 m² g⁻¹ for Pd/NiCrO₄, respectively. The SEM analysis showed the typical spongy structure for both the catalytic materials, enlightening a nanometric porosity formed during the SCS preparation, responsible for the high BET values. The T₅₀ values of the as-prepared catalysts from the TPO analysis are reported in Fig. 2. Both the catalysts lowered the T₅₀: 2% Pd/CeO₂-2ZrO₂ catalyst appeared as the most promising one, thanks to its lowest T₅₀.

![Fig. 2 CH₄ conversion vs T for the as-prepared catalysts.](image)

3.2. Kinetics analysis

For both catalysts, the present kinetic study is based on the data of CH₄ reaction rate (R_{CH₄} in mol CH₄ s⁻¹ g⁻¹) obtained at steady-state mode, operating the reactor under a differential regime of CH₄ conversion (< 0.15) and calculated according to:

\[ R_{CH₄} = \frac{F_{fed} \cdot \Delta CH₄}{M_{cat}} \]

where F_{fed} is the fed flow rate to the differential reactor, \( \Delta CH₄ \) is the reacted CH₄ and M_{cat} the amount of catalyst loaded into the reactor. For both catalysts, the absence of mass transfer
limitations at reaction conditions was verified both experimentally and theoretically. The external diffusion mass transfer resistance was evaluated theoretically and found negligible. Mars van Krevelen (MvK) models are the most frequently used to describe the oxidation of organic compounds over noble metals as well as over many metal oxides. Among noble metals, MvK mechanisms are likely to occur for Pd and Rh, since it was observed that they present different interchangeable catalytically active oxidation states at the reaction conditions used for HCs oxidation [15]. Various MvK mechanisms exists in literature. According to these models, the reaction takes place through alternative oxidations and reductions of the catalyst surface, the surface oxidation being produced by molecular oxygen dissociatively adsorbed from the gas phase [15]. The CH$_4$ reacts with the chemisorbed atomic oxygen in successive irreversible steps, yielding finally the total oxidation products and making free the corresponding site fraction:

\[
O_2 + \theta \rightarrow \theta_{O2} \rightarrow 2\theta_O \\
CH_4 + \theta_O \rightarrow \theta_I \rightarrow \text{products} + \theta
\]  

Concerning the 2% Pd/CeO$_2$$\cdot$2ZrO$_2$ catalyst, the best kinetics law for data fitting was the MvK mechanism taking into account the concentration of molecular O$_2$ adsorbed on the catalyst surface [15]:

\[
R_{\text{CH}_4} = \frac{k_1 k_2 \cdot p_{\text{CH}_4} p_{O2}}{k_3 p_{\text{CH}_4} + k_2 p_{O2}} \left(1 - \frac{k_1 p_{O2}}{k_1'}\right)
\]  

where $k_1$ [mol g$^{-1}$ s$^{-1}$ bar$^{-1}$] is the rate constant for the molecular O$_2$ adsorption, $k_2$ [mol g$^{-1}$ s$^{-1}$ bar$^{-1}$] is the rate constant for the reaction between CH$_4$ and adsorbed molecular O$_2$ and $k_1'$ [mol g$^{-1}$ s$^{-1}$] is the rate constant for adsorbed molecular O$_2$ dissociation. The reaction kinetics constants $k_1$, $k_2$ and $k_1'$ can be expressed as a function of T by Arrhenius expression:

\[
k_i = k_i^\infty \cdot \exp\left(-\frac{E_i}{RT}\right)
\]

Table 1 lists all the values of the kinetics parameters derived on the basis of the described kinetic expressions, by least-squares fitting of the experimental data. On the basis of the latter, other considered kinetics mechanisms for the 2% Pd/CeO$_2$$\cdot$2ZrO$_2$ catalyst, i.e. other MvK, Langmuir-Hinshelwood or Eley-Rideal, led in this specific case to thermodynamically inconsistent adsorption heats and activation energies, or negative kinetic parameters. Some representative diagrams concerning experimental data vs. model predictions are then reported in Figs. 3 and 4.

<table>
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<tr>
<th>Tab. 1</th>
<th>Kinetic values determined for 2% Pd/CeO$_2$$\cdot$2ZrO$_2$ catalyst.</th>
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<tr>
<td>$E_1$</td>
<td>62 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>75 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$E'_1$</td>
<td>14 kJ mol$^{-1}$</td>
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For the 2% Pd/NiCrO$_4$ catalyst, the effect of the O$_2$ concentration on the reaction rate was too weak to obtain accurate data concerning the adsorption coefficient $K_{O2}$ based on Van’t Hoff expression. Then, a simpler CH$_4$ rate equation (first-order dependence vs. CH$_4$ partial pressure and zero-order vs. O$_2$ one) was successful used for this catalyst:

\[
R_{\text{CH}_4} = k \cdot p_{\text{CH}_4}
\]
Fig. 3  $R_{CH_4}$ vs. $p_{CH_4}$ at different operating $T$ values for the 2% Pd/CeO$_2$·2ZrO$_2$ catalyst: experimental data (points) and model predictions (solid lines).

Fig. 4  $R_{CH_4}$ vs. $p_{O_2}$ at different operating $T$ values for the 2% Pd/CeO$_2$·2ZrO$_2$ catalyst: experimental data (points) and model predictions (solid lines).

Fig. 5  $R_{CH_4}$ vs. $p_{CH_4}$ at different operating $T$ values for the 2% Pd/NiCrO$_4$ catalyst: experimental data (points) and model predictions (solid lines).

In such equation, the above expression (4) is still valid for the kinetic constant $k$ [mol g$^{-1}$ s$^{-1}$ bar$^{-1}$]. The activation energy in this case was calculated as 83.9 kJ mol$^{-1}$ and the pre-exponential factor as 52.6 kmol g$^{-1}$ s$^{-1}$ bar$^{-1}$. A representative diagram concerning
experimental data vs. model predictions is reported in Fig. 5: the data points in this last figure appear assembled into groups, which originate from runs performed at equal CH$_4$ feed concentration and different O$_2$ feed concentrations (2-15%). In this case, the active sites for O$_2$ chemisorption present on the catalyst surface are saturated over the entire range of temperatures (380-580 °C) and O$_2$ partial pressure (2-15%) used in the present study.

4. Conclusions

Pd based catalysts carried by both CeO$_2$·ZrO$_2$ and NiCrO$_4$ were prepared by solution combustion synthesis, characterized and tested for CH$_4$ catalytic combustion. A kinetic study on the above supported Pd-based catalytic materials showed that for 2% Pd/ CeO$_2$·ZrO$_2$ catalyst the most suitable model fitting the experimental data was the Mars van Krevelen mechanism taking into account the concentration of molecular O$_2$ adsorbed on the catalyst surface, whereas for 2% Pd/NiCrO$_4$ the reaction was first order towards CH$_4$ concentration and the active sites for O$_2$ chemisorption on catalyst surface were saturated over the entire range of investigated temperatures and O$_2$ partial pressures. For both catalysts, the obtained activation energy values were inside the range reported for similar catalysts in literature.

5. References