Development of technology of methane combustion on granulated catalysts for environmentally friendly gas turbine power plant

Boreskov Institute of Catalysis, Novosibirsk, Russia

V.M.Zakharov, B.I.Braynin, G.K.Vedeshkin, E.D.Sverdlov, O.N.Favorski
Central Institute of Aviation Motors, Moscow, Russia
The Boreskov Institute of Catalysis (BIC) is one of the largest research centers worldwide specialized in catalysis. The BIC’s R&D activities span the areas from fundamental problems of catalysis to development of new catalysts and catalytic technologies, including catalytic combustion.

The Baranov Central Institute of Aviation Motors (CIAM) is leading establishment of the Russia aviation engine - building for provision of world-level basic and applied research, creation of scientific and technological base for development of new "critical" technologies – gas turbine power units.

Development advanced environment friendly gas turbine with catalytic combustion chamber
Airplane engines designed at CIAM

A-50 (powered by D-30KP)  IL-78 (powered by D-30KP)
CIAM – the only research organization realizing integral scientific studies and development in the field of aero engines - from fundamental studies of physical processes up design of new engines, certification, as well as scientific support of their operation by reliability and failures. Practically all Soviet (Russian) aircraft engines were created under direct participation of Institute and passed upgrading at CIAM facilities.

Large scale engine and turbine testing facilities of CIAM
BIC and CIAM in Russia

Moscow (CIAM)

St-Petersburg

Omsk

Novosibirsk (BIC)

Volgograd
The goal

Development of catalyst and catalytic combustion chamber for small gas turbine power plants for decentralized power supply

Approach

- Regenerative turbine technology
- Low temperature turbine
- Granulated catalyst for stationary turbine loading

Key steps

1) development and study of advanced granulated catalysts with low Pd content, providing minimum emissions of NO\textsubscript{x} (<5 ppm), CO (<5 ppm) and HC (5 ppm)

2) modeling of the processes in a catalytic combustor

3) design of a model catalytic combustion chamber and pilot testing

4) design and testing of a prototype catalytic combustion chamber
Catalysts for high-temperature combustion of hydrocarbon fuel

1. Catalysts based on noble metals
   - Pd
   - Most active in deep oxidation of methane, CO, unsaturated hydrocarbons
   - Low light-off temperature
   - Stable to thermal sintering in the oxidizing environment
   - The upper temperature limit of their use is about 800-900°C
     PdO → Pd

2. Catalysts based on transition metal oxides
   - MnOx
   - MnLaAl11O19
   - MnLaAl11O19 has high thermal stability
   - The thermal stability of MnOx/Al2O3 catalysts can be increased (up to 1300°C) by doping with La, Mg or Ce oxides
   - Inexpensive

For oxidation of methane, MnOx/Al2O3 and hexaaluminates are less active at low temperature than Pd/CeO2-Al2O3 catalysts

The properties of these two catalyst-types will be used for development of the combined catalytic package with reduced Pd content for combustion chamber,
1.1. Development of catalyst with low ignition temperature

Pd Catalysts supported on $\gamma$-Al$_2$O$_3$

**Preparation conditions**

1. **Type of active component**
   - Pd 0.1 - 2 wt.%
   - CeO$_2$ 3 - 12 wt.%

2. **Loading of active component**
   - Pd(NO$_3$)$_2$
   - Pd(CH$_3$COO)$_2$
   - Pd(NH$_3$)$_4$(NO$_3$)$_2$
   - Pd(NH$_3$)$_4$(Cl$_3$)$_2$

3. **Precursor**

4. **Calcination temperature**
   - 800 °C – 1100°C

5. **Characterization**

- XRD
- TPR-H$_2$
- X-ray microanalysis

Catalytic activity in methane oxidation

- Space velocity: 1000 and 24000 h$^{-1}$
- Temperature: 200 – 700°C
- Feed composition: 1 vol.% in air
1.2. Development of catalyst with high thermal stability

Oxide and mixed Catalysts supported on $\gamma$-Al$_2$O$_3$

**Preparation conditions**

1. Type of active component

- MnO$_x$ and MnLaAl$_{11}$O$_{19}$
- Pd and MnO$_x$, MnLaAl$_{11}$O$_{19}$

2. Loading of active component

- MnO$_2$ - 3 - 11 wt.%
- La$_2$O$_3$ - 5 - 22 wt.%
- Mn(NO$_3$)$_3$
- Mn(CH$_3$COO)$_2$

- Pd 0.1 - 2 wt.%

3. Precursor

- H$_2$PdCl$_4$
- Pd(NO$_3$)$_2$
- Pd(CH$_3$COO)$_2$

4. Calcination temperature

- 900 °C – 1100°C

5. Characterization

- XRD
- TPR-H$_2$
- X-ray microanalysis

Catalytic activity in methane oxidation

- Space velocity: 1000 and 24000 h$^{-1}$
- Temperature: 200 – 700°C
- Feed composition: 1 vol.% in air
## Properties of granulated catalysts

**Ring size:**
- Length – 7.5 mm
- OD– 7.5 mm
- ID – 2.5 mm

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tcalc.</th>
<th>Loading wt.%</th>
<th>XRD composition</th>
<th>$S_{sp}$ m$^2$/g</th>
<th>$V_{\Sigma}$ cm$^3$/g</th>
<th>Strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IC-12-60-2</strong></td>
<td>1000</td>
<td>Pd- 2.1</td>
<td>$\delta$-$\text{Al}_2\text{O}_3$</td>
<td>74</td>
<td>0.26</td>
<td>2.4</td>
</tr>
<tr>
<td>Pd-Ce-$\text{Al}_2\text{O}_3$</td>
<td></td>
<td>Ce- 10.1</td>
<td>$\text{CeO}<em>2$ D $\sim$ 200Å ($S</em>{33}$=1100)* $\text{PdO}$ D $\sim$ 180 and 250Å ($S_{39}$=480)*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ICT-12-40</strong></td>
<td>900</td>
<td>Mn – 6.9</td>
<td>$(\delta+\gamma)$-$\text{Al}_2\text{O}_3$ and $\alpha$-$\text{Al}_2\text{O}_3$ $\text{Mn}_2\text{O}_3$</td>
<td>80</td>
<td>0.23</td>
<td>2.3</td>
</tr>
<tr>
<td>$\text{MnO}_x$-$\text{Al}_2\text{O}_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>IC-12-61</strong></td>
<td>1100</td>
<td>Mn-6.9</td>
<td>$\text{MnLaAl}<em>{11}\text{O}</em>{19}$ ($S_{37}$=60)* $\text{LaAlO}_3$ $\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>43</td>
<td>0.18</td>
<td>3.4</td>
</tr>
<tr>
<td>$\text{Mn-La-Al}_2\text{O}_3$</td>
<td></td>
<td>La-10.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>IC-12-62-2</strong></td>
<td>1000</td>
<td>Pd -0.65</td>
<td>$\text{MnLaAl}<em>{11}\text{O}</em>{19}$  ($S_{37}$ = trace)* $\gamma^\ast$-$\text{Al}_2\text{O}<em>3$ ($a$ $\sim$ 7.937 Å) $\text{PdO}$ D $\sim$400 Å ($S</em>{39}$ - 70)</td>
<td>48</td>
<td>0.18</td>
<td>2.5</td>
</tr>
<tr>
<td>Pd-Mn- $\text{LaAl}_2\text{O}_3$</td>
<td></td>
<td>Mn-7.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>La- 9.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The catalyst IC-12-60 based on Pd-CeO$_2$-Al$_2$O$_3$ was selected as a catalyst with low ignition temperature:

- the methane ignition temperature on the catalyst is 240°C, the combustion products do not contain CO and NO$_x$
- the active component is highly dispersed PdO particles which provide high activity at low temperatures

This catalyst can be used in the upstream section of combustion chamber for initiation of fuel combustion
1.2. Optimization of catalyst with high thermal stability

Catalytic activity of Pd-Mn catalyst: Effect of Pd precursor

- At the same Pd loading (1.5 wt.%) the magnitude of the synergetic effect depends on the palladium precursor: acetate, nitrate or chloropalladic acid.
- The Pd loading (0.5 wt.%), Pd precursor (nitrate) and calcination temperature (1000°C) were optimum for Pd-Mn catalysts.
1.2. Optimization of catalyst with high thermal stability

Stability of Mn-La and Pd-Mn-La catalyst at high temperature

- The catalysts IC-12-61 containing Mn-La hexaaluminate structure exhibits high stability at high temperatures.

- Doping of Mn-La catalyst (IC-12-62) with Pd to 0.5 wt.% allows a decrease of ignition temperature by 100°C and reduction of CO content in the reaction products.

- These catalysts can be used in the downstream section of the combustion chamber for high temperature fuel combustion.
2. Modeling of processes in a catalytic combustor
2.1. Calculation of kinetic parameters from experimental data

Total rate of methane oxidation

\[ w = k_0 (1 - \varepsilon) \exp\left(-\frac{E}{RT}\right) C_{\text{CH}_4} \left(\frac{P}{P_0}\right), \]

\( k_0 \) – pre-exponential factor of rate constant (s\(^{-1}\)), \( E \) – activation energy (J/mol), \( R \) – absolute gas constant (J mol\(^{-1}\) K\(^{-1}\)), \( T \) – reaction temperature (K), \( \varepsilon \) – part of free volume in catalyst bed, \( C_{\text{CH}_4} \) – methane concentration (mole fraction), \( P \) – pressure (atm), \( P_0 \) – standard pressure (1 atm).

Kinetic parameter of deep methane oxidation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( k_0 ), s(^{-1})</th>
<th>E, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC-12-60 (Pd-Ce-Al(_2)O(_3))</td>
<td>4.36 \cdot 10^7</td>
<td>81.4</td>
</tr>
<tr>
<td>ICT-12-40 (Mn-Al(_2)O(_3))</td>
<td>1.09 \cdot 10^5</td>
<td>71.2</td>
</tr>
<tr>
<td>IC-12-61 (Mn-La-Al(_2)O(_3))</td>
<td>1.09 \cdot 10^5</td>
<td>71.2</td>
</tr>
<tr>
<td>IC-12-62 (Pd-Mn-La-Al(_2)O(_3))</td>
<td>3.29 \cdot 10^5</td>
<td>63.8</td>
</tr>
</tbody>
</table>
2.2. Design of catalyst packages in the combustion chamber

Uniform catalyst package

Combined catalyst packages
2.2 Modeling of methane combustion process on uniform catalyst package

Combustion efficiency as function of methane concentration and GHSV

Catalyst package: ICT-12-40 (MnOₓ-Al₂O₃) or IC-12-61(Mn-La-Al₂O₃)

\( C_{\text{CH}_4} = 1.5 - 5.0 \ \text{vol.\%}, \ \text{GHSV} = 7000 - 40000 \ \text{h}^{-1}, \ P = 1 \ \text{atm} \)

The methane combustion efficiency increases with the increase of the temperature and with methane concentration.
2.3. Modeling of methane combustion process on combined catalyst package

Temperature profile in the catalyst bed and methane conversion profile as function of GHSV

Catalyst package: IC-12-60 (Pd-Ce-Al₂O₃)- 20 mm + IC-12-61(Mn-La-Al₂O₃)-180 mm

- The temperature growth in catalyst bed and the methane conversion growth are higher in IC-12-60 catalyst bed than in IC-12-61 catalyst bed
2.3. Modeling of methane combustion process on combined catalyst package

Effect of ratio of heights of IC-12-60 and IC-12-62 catalyst beds and GHSV on methane conversion

Catalytic package: IC-12-60 (2%Pd-Ce-Al₂O₃) + IC-12-62 (0.5%Pd-Mn-La-Al₂O₃)

Inlet temperature - 450°C,
Inlet methane concentration - 1.5 vol.%, pressure – 1 atm

- The methane combustion takes place mainly in IC-12-60 catalyst bed
- This tendency becomes stronger with the decreasing space velocity and the increasing of the height of IC-12-60 catalyst bed
2.3. Modeling of methane combustion process on combined catalyst package

Combustion efficiency as function of ratio between height of the catalyst bed and GHSV

Catalyst package: IC-12-60 (Pd-Ce-Al$_2$O$_3$) + IC-12-61(Mn-La-Al$_2$O$_3$)

The methane combustion efficiency increases with the increase of the height of IC-12-60 catalyst bed and with methane concentration.
2.3 Modeling of methane combustion process on combined catalyst package

Effect of height ratio of IC-12-60/IC-12-62 catalyst beds on parameters of methane combustion

Catalytic package: IK-12-60 (2%Pd-Ce-Al$_2$O$_3$) + IK-12-62 (0.5%Pd-Mn-La-Al$_2$O$_3$)

Inlet temperature - 450°C,
Inlet methane concentration - 1.5% vol., pressure – 1 atm

The methane combustion efficiency and temperature in catalyst bed increase with the increase of the height of IC-12-60 catalyst bed
2.3. Modeling of methane combustion process on combined catalyst package

Effect of shape and size of catalyst granules on parameters of methane combustion process

Catalyst package: IC-12-60 (2%Pd-Ce-Al₂O₃)-20 mm + IC-12-62 (0.5%Pd-Mn-La-Al₂O₃)-180 mm

Inlet temperature - 450ºC, inlet methane concentration - 1.5% vol., pressure – 1 atm

Granule shape - ring

The methane combustion efficiency and the pressure drop in catalyst bed increase with the decrease of the granule size
3. Design of catalyst packages in the combustion chamber

- Uniform catalyst package
- Combined catalyst packages

\[ \text{CH}_4 + \text{air} \]
3. Design of catalyst packages in the combustion chamber

Schematic view of two-step methane oxidation in catalytic combustion chamber

**«ignition region»**
Pd-catalyst with low light-off temperature - 240°C initiates methane oxidation and provides outlet temperature sufficient to start methane combustion on the oxide catalyst

**«high temperature region»**
thermostable oxide catalyst, Mn-La-Al₂O₃, provides stable methane combustion at high temperatures

**Catalytic activity in methane conversion**
Pd-Ce-Al₂O₃-catalyst

Mn-La-Al₂O₃-catalyst:
- initial; □- after 30 h; ○- 50 h; ▲- 100 h testing at 930°C

CH₄+air

CH₄+air

T<1000K

T=1200K
4. Tests in a model catalytic combustion chamber

Scheme of the model catalytic combustion chamber (BIC)
4. Testing of uniform catalytic package in the model catalytic combustor

GHSV - 15000 h\(^{-1}\), \(\alpha\) - 6.8-7.0, CH\(_4\) – 1.5 vol.%

- The Mn-La catalyst which contains hexaaluminate structure exhibits higher stability at high temperatures than MnO\(_x\)-Al\(_2\)O\(_3\) catalyst

- Doping of Mn-La catalyst with palladium to 0.5 wt.% allows an increase of methane combustion efficiency (from 99.3 to 99.5%) and a decrease of inlet temperature (from 600 to 575°C)
4. Testing of combined catalytic package in the model catalytic combustor

GHSV - 15000 h\(^{-1}\), \(\alpha\) - 6.8-7.0, CH\(_4\) – 1.5 vol.%

Catalyst package formed by two beds of catalysts of the same chemical composition: the upstream bed of large rings and the downstream bed of smaller beads (with different void volumes) allows a considerable increase of combustion efficiency
4. Testing of combined catalytic package in a model catalytic combustor

GHSV - 15000 h\(^{-1}\), \(\alpha\) - 6.8-7.0, CH\(_4\) – 1.5 vol.\%

![Graph showing CH\(_4\) conversion vs time duration.]

Composing the catalyst package by three catalysts with different chemical compositions and different shapes:

- IC-12-60 (ring) with low ignition temperature
- IC-12-61 (ring) with high thermal stability
- IC-12-62 (sphere) smaller granules and high activity

allowed us to achieve high combustion efficiency at a low inlet temperature 470\(^\circ\)C
4. Tests in a model catalytic combustion chamber

Scheme of the model catalytic combustion chamber (CIAM)

1 – catalytic combustion chamber
2 – thermal shield
3 – air electric heater
4 – compensating lattice
5 – electric heater
6 – «guard» electric heater
7 – thermal protection of frame
8 – mixer
9 – hot probe

Sampling

Combustion Products
4. Testing of combined catalytic package in the model catalytic combustion chamber

Design of catalytic combustion chamber

Catalyst bed height – 300 mm
Combination of beds: IC-12-60 (Pd-Ce-Al₂O₃) - 20mm
Inert material – 20 mm
IC-12-61 (Mn-La-Al₂O₃) - 260mm

Temperature profile through catalyst bed (α=6.68-10)

Outlet concentrations of CH, CO, NOx (α=6.68-10)

The layer of inert material acts as a heat shield. At different methane concentrations and low air/fuel equivalence ratio (α = 6.7), the Pd-catalyst is not overheated above 1000K (730°C).

Concentrations of emissions at the outlet of the catalytic combustion chamber are NOₓ 0-1 ppm; CO < 4 ppm; CH <10 ppm
5. Testing of the prototype catalytic combustion chamber

Schematic view and main characteristics of the prototype catalytic combustor for a 125 kW gas turbine

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>0.6 m</td>
</tr>
<tr>
<td>Height</td>
<td>1.65 m</td>
</tr>
<tr>
<td>Catalyst loading</td>
<td>70 kg (87 dm³)</td>
</tr>
<tr>
<td>Temperature at the combustor inlet</td>
<td>830 K</td>
</tr>
<tr>
<td>Temperature at the combustor outlet</td>
<td>1180 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>5 atm</td>
</tr>
<tr>
<td>Air velocity at the combustor inlet</td>
<td>950 g/s (2640 nm³/h)</td>
</tr>
</tbody>
</table>
Photos of the prototype catalytic combustor for a 125 kW gas turbine
5. Testing of the prototype catalytic combustion chamber

Design of catalytic combustion chamber

Catalyst: ICT-12-40 (Mn-Al$_2$O$_3$)
Catalyst bed height – 450 mm
Catalyst bed volume – 87 dm$^3$
Granule shape – ring
Granule size – 7.5 x 7.5 x 2.5 mm

Test conditions

Temperature at the combustor inlet 850 K
Pressure at the combustor inlet 5 atm
Air flow velocity at the combustor inlet 830 g/s (2310 nm$^3$/h)
Methane flow velocity in the preheating chamber 0-0.9 g/s (0-4.5 nm$^3$/h)
Methane flow velocity in the combustor 6.9-7.5 g/s (34.8-37.5 nm$^3$/h)
GHSV 19000 - 31200 h$^{-1}$
## 5. Testing of the prototype catalytic combustion chamber

### Results of the tests of the prototype catalytic combustor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature at the combustor inlet</td>
<td>850 K</td>
</tr>
<tr>
<td>Pressure at the combustor inlet</td>
<td>5.0 atm</td>
</tr>
<tr>
<td>Air flow velocity at the combustor inlet</td>
<td>830 g/s (2310 nm(^3)/h)</td>
</tr>
<tr>
<td>Methane flow velocity in the preheating chamber</td>
<td>0-0.9 g/s (0-4.5 nm(^3)/h)</td>
</tr>
<tr>
<td>Methane flow velocity in the combustor</td>
<td>6.9 g/s (34.5 nm(^3)/h)</td>
</tr>
<tr>
<td>GHSV</td>
<td>27000 h(^{-1})</td>
</tr>
<tr>
<td>Temperature at the catalyst bed inlet</td>
<td>835 - 860 K</td>
</tr>
<tr>
<td>Temperature at the catalyst bed outlet</td>
<td>1145-1160 K</td>
</tr>
<tr>
<td>Concentrations at the combustor outlet</td>
<td></td>
</tr>
<tr>
<td>HC</td>
<td>18-20 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>4.2-6 ppm</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>0 ppm</td>
</tr>
</tbody>
</table>
5. Testing of the prototype catalytic combustion chamber

CO, NOx and CH₄ concentrations (ppm) at the outlet of the catalytic combustion chamber

- CO concentration: 5 – 6 ppm
- NOx concentration: 0 ppm
- CH₄ concentration: 18-20 ppm
5. Testing of the **modified** prototype catalytic combustion chamber

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature at the combustor inlet</td>
<td>840 K</td>
</tr>
<tr>
<td>Pressure at the combustor inlet</td>
<td>5.0 atm</td>
</tr>
<tr>
<td>Air flow velocity at the combustor inlet</td>
<td>960 g/s (2670 nm³/h)</td>
</tr>
<tr>
<td>Methane flow velocity in the preheating chamber</td>
<td>0.89 g/s (4.5 nm³/h)</td>
</tr>
<tr>
<td>Methane flow velocity in the combustor</td>
<td>7.45 g/s (37.5 nm³/h)</td>
</tr>
<tr>
<td>GHSV</td>
<td>31200 h⁻¹</td>
</tr>
<tr>
<td>Temperature at the catalyst bed inlet</td>
<td>880 K</td>
</tr>
<tr>
<td>Temperature at the catalyst bed outlet</td>
<td>1145 K</td>
</tr>
<tr>
<td>Concentrations at the combustor outlet</td>
<td></td>
</tr>
<tr>
<td>HC</td>
<td>6 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>4.2 ppm</td>
</tr>
<tr>
<td>NOₓ</td>
<td>4.6 ppm</td>
</tr>
</tbody>
</table>
First Snow in Novosibirsk. October 2007
(the same we had this year on 17 September 2008)