

## Study of Catalysts for Catalytic Burners for Fuel Cell Power Plant Reformers

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(Received 4 September 2002 • accepted 22 November 2002)

**Abstract**—Catalytic burners for fuel cell power plant reformers are alternatives to conventional flame burners. Their application is expected to provide uniform temperatures in the reformer, efficient use of low-calorific gaseous by-products and reduction of pollutant emissions. For testing in the burners, a series of spherical Pd/CeO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared. An optimum concentration of ceria providing the highest thermal stability of catalysts was determined. An effect of catalyst activation in the reaction mixture-1% methane in air was observed. A series of Mn containing oxide catalysts on spherical  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or ( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub>, both pure and doped with La, Ce and Mg oxides were prepared. The catalysts were characterized by chemical analysis, X-ray phase analysis, BET surface area and activity measurements in methane oxidation. A batch of Mn-Mg-La-Al-O catalyst was prepared for further long-term testing in a model reformer with a catalytic burner. A model reformer with a catalytic burner was designed and fabricated for testing in the composition of the bench-scale Fuel Cell Power Plant. Preliminary testing of this catalyst showed that it provided complete methane combustion at the specified operational temperatures over 900 °C.

**Key words:** Fuel Cell, Catalytic Burner, Reformer, Catalytic Combustion, Methane, Pd-Ceria, Alumina, Alumina Stabilization by La, Ce, Mg, Manganese Oxide Catalysts

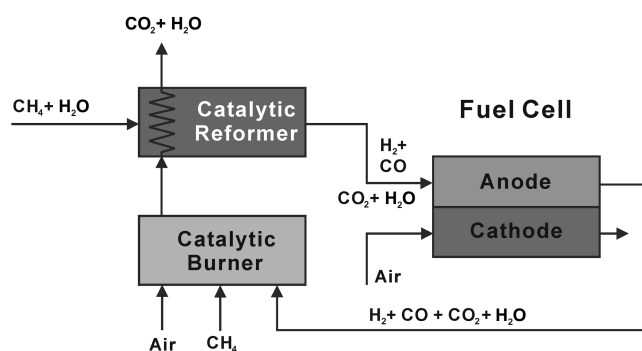
### INTRODUCTION

Fuel Cell Power Plants (FC PP) are very attractive novel energy generating systems, which keep the environment clean and save energy resources [Williams, 1996]. The initial fuel for use in FC PP is natural gas or methane. Natural gas is subjected to the catalytic reforming in the Power Plant fuel conditioning system, where it is converted into a hydrogen-rich gas mixture used in an FC stack for electrochemical reaction of hydrogen oxidation.

A functioning FC stack produces a gas mixture (the anode gas), which contains a certain amount of combustible components, such as hydrogen, carbon monoxide, and methane residue. This mixture is burned in order to obtain heat required for the PP internal consumption, thus increasing the PP efficiency.

Usually, flame combustion of methane is used in the PP fuel conditioning system to provide heat for endothermic steam reforming reaction of natural gas. However, the use of flame burners in the reformers results in overheating of the walls of heat absorbing elements of the reformer reactor, thus reducing considerably the PP service life. Another serious drawback of flame combustion is formation of nitrogen oxides and products of incomplete combustion: CO, HCOH, and soot.

The alternative to flame combustion is flameless catalytic combustion. This process has received increasing attention in the last decades for numerous applications due to its potential for reducing pollutant emissions, most notably nitrogen oxides. It also provides



**Fig. 1. Schematic representation of a catalytic burner combined with a fuel cell power plant.**

the possibility to burn low calorific fuels, such as anode gases, under stable regimes and with high efficiency.

A schematic representation of the proposed concept of a catalytic burner installed in the fuel cell power plant is shown in Fig. 1.

The main goal of the present work is the study of catalysts to be used in burners for FC PP reformers.

For achieving this goal the following tasks should be accomplished:

- development of highly effective stable catalysts operating at high temperatures 1,000-1,200 °C;
- characterization and testing of the developed catalysts in laboratory conditions;
- design and fabrication of the reformer with a prototype catalytic burner;
- testing of the reformer with a prototype catalytic burner.

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In this work, both noble metal and metal oxide catalysts have been prepared and studied.

Noble metals initiate combustion processes at rather low temperatures; however their application at elevated temperatures is limited due to the high volatility of vapors of oxides of most of these metals [Arai et al., 1986]. Depositing noble metals on the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) improves operational properties (in the case of Pd, thermal stability is also increased), but still the limit of application for such systems is an operational temperature of not more than 1,000 °C. It is known that the optimum support for catalyst preparation is  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, because of its structural-mechanical properties: large BET surface area and pore volume and high mechanical strength. Thermal stability of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be increased by introduction of rare earth metal additives providing both stabilization of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase [Ismagilov et al., 1999; Shkrabina et al., 1986] and resistance of the active component to sintering [Frey et al., 1994].

Pd-ceria-alumina system is known to be active as a three-way automotive catalyst [Fernandez-Garcia et al., 2001] and as a catalyst for methane oxidation [Groppi et al., 1999]. The presence of ceria in Pd/Al<sub>2</sub>O<sub>3</sub> was shown to improve the catalyst durability in methane combustion increasing PdO resistance to sintering and decreasing of the PdO transformation kinetics into less active Pd [Euzen et al., 1999]. Therefore, it was of interest to prepare alumina supported Pd-ceria catalysts with various ceria contents and to study their properties and activity in methane oxidation to find an optimum catalyst formula for further testing in catalytic burners for fuel cell reformers.

Alumina supported manganese oxide catalysts are also promising for high temperature methane combustion. These catalysts retain the initial activity in hydrocarbon oxidation up to 1,000 °C, and further increase of thermal stability of the catalysts (to 1,100-1,300 °C) can be achieved by catalyst doping with modifying agents (La, Ce and Mg oxides) [Tsykoza et al., 1996, 1997; Ismagilov et al., 1997]. A series of Mn containing oxide catalysts on spherical (1.4-1.8 mm)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ( $\gamma$ - $\chi$ )-Al<sub>2</sub>O<sub>3</sub>, pure or doped with La, Ce and Mg oxides were prepared for studies in methane combustion reaction.

## EXPERIMENTAL

### 1. Pd-Ceria Catalysts

Spherical  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared according to hydrocarbon-ammonia

method from reprecipitated aluminum hydroxide [Shepeleva et al., 1990; Ismagilov et al., 1997] was used for catalyst synthesis.

The modification of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by Ce ions (2-15 wt%) as CeO<sub>2</sub> was performed by wetness impregnation with aqueous solutions of cerium nitrate. Then the samples were dried under IR heater and calcined at 600 °C for 4 h.

The active component was deposited by wetness impregnation of the modified support with a solution of H<sub>2</sub>PdCl<sub>4</sub>, then the catalysts were dried and calcined at different temperatures 600, 800, 900, 1,000 °C for 4 h.

The catalysts calcined at 1,000 °C were additionally treated for 3-6 h in the reaction mixture (1% CH<sub>4</sub>+air) in a flow reactor at GHSV = 1,000 h<sup>-1</sup>.

### 2. Mn-Al-O Catalysts

Mn-Al-O catalysts were prepared by wetness impregnation of the support with aqueous solutions of manganese nitrate, with subsequent drying and calcination in air at 900 °C for 4 h. The content of manganese in the main series of catalysts (calculated as MnO<sub>2</sub>) was ~5 wt%. For comparison, a sample with 10 wt% of manganese was also prepared.

The supports used were spherical  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and spherical (75%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>+25%  $\chi$ -Al<sub>2</sub>O<sub>3</sub>) prepared from hydroxide of pseudoboehmite structure obtained from amorphous alumina produced by the method of pulse thermal gibbsite decomposition [Ismagilov et al., 1999] and ( $\gamma$ - $\chi$ )-Al<sub>2</sub>O<sub>3</sub> modified with Mg ions. The calcination temperature of all initial supports is 550 °C. The main characteristics of the supports (BET surface area, pore structure) are similar. The modification of supports with oxides of La and Ce was conducted according to [Shepeleva et al., 1990]. The characteristics of the initial and modified supports are given in Table 1.

### 3. Catalyst Characterization

The activity of the catalysts was studied in the reaction of methane oxidation in the temperature range 100-600 °C under the following conditions:

- catalyst volume 0.8 cm<sup>3</sup>,
- gas flow rate 13.3 cm<sup>3</sup>/min (1,000 h<sup>-1</sup>),
- the composition of the gas mixture 1 vol% CH<sub>4</sub>, balance air.

The composition of the reaction products was determined by GC. The catalyst activity was characterized by the temperature of methane 50% conversion to deep oxidation products at the temperature increasing from 100 to 600 °C and at the temperature decreasing

**Table 1. Characteristics of spherical alumina supports**

#	Initial support	Additive (~5 wt%)	$S_{BET}$ , m <sup>2</sup> /g 900 °C	XRD samples calcined at 900 °C
1	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	-	170	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>
2	The same	La <sub>2</sub> O <sub>3</sub>	146	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> <sup>1)</sup>
3	The same	CeO <sub>2</sub>	168	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> <sup>1)</sup> + CeO <sub>2</sub>
4	75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> + 25% $\chi$ -Al <sub>2</sub> O <sub>3</sub>	-	190	75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> + 25% $\chi$ -Al <sub>2</sub> O <sub>3</sub>
5	The same	La <sub>2</sub> O <sub>3</sub>	163	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> <sup>1)</sup>
6	The same	CeO <sub>2</sub>	163	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> <sup>1)</sup> + CeO <sub>2</sub>
7	4.5% MgO/(75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> + 25% $\chi$ -Al <sub>2</sub> O <sub>3</sub> )	-	181	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> <sup>2)</sup>
8	The same	La <sub>2</sub> O <sub>3</sub>	171	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> <sup>2)</sup>
9	The same	CeO <sub>2</sub>	181	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> <sup>2)</sup> + CeO <sub>2</sub>

$\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>1)</sup>-diffractogram shows predominant presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>2)</sup>-low temperature solid solution based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure containing Mg or Mg and La ions.

from 600 to 100 °C- $T'_{50\%}$  and  $T^D_{50\%}$ , respectively.

## RESULTS AND DISCUSSION

### 1. Pd-Ceria Catalysts

The compositions of the catalysts prepared and their properties depending on the amount of CeO<sub>2</sub> introduced and the calcination temperature are given in Table 2.

It can be seen that the increase of ceria content in the catalyst samples calcined at 600 °C leads to reduction of the BET area. How-

ever, at higher catalyst calcination temperatures the dependencies of the BET area on the ceria content become more complex and have maxima at a certain ceria content. This can be caused by sintering processes and phase transformations.

Of the catalysts studied, the one containing 12 wt% of CeO<sub>2</sub> has the highest thermal stability. As the CeO<sub>2</sub> content is increased to 15 wt% the thermal stability starts to decrease. This can be caused by the substantial surface coverage by CeO<sub>2</sub> crystals.

The XRD data indicate that the samples with a high ceria content 12-15 wt% surpass the samples with low ceria content (0-5%) by their thermal stability. Table 2 shows that the samples with a low CeO<sub>2</sub> content as well as the ones on the "pure" support at temperatures as low as 900 °C exhibit the formation of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> phase. At a further increase of the temperature to 1,000 °C the formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> takes place: in significant amounts (~25%) in the samples based on the "pure" support and in trace amounts in the samples containing 2-5 wt% CeO<sub>2</sub>. In the samples containing 12-15 wt% of CeO<sub>2</sub>, alumina is present in  $\gamma$  and  $\theta$ -modifications at 900 and 1,000 °C, respectively.

Ceria in all samples is formed as well-crystallized CeO<sub>2</sub>, with the particle size rising from 75 to 250 Å at the calcination temperature increase from 600 to 1,000 °C. The PdO phase is not detected in all 600 °C samples and in 800 °C samples with high ceria content due to the high dispersity of PdO. As the calcination temperature is increased the diffractograms reveal the appearance of PdO lines corresponding to roughly dispersed phase with the particle size of 200-300 Å.

The XRD study of the sample containing 12 wt% CeO<sub>2</sub> (#19, Table 2) after its treatment in the reaction mixture for 6 h and after its sintering in air at a temperature of 1,000 °C for 25 h revealed only minor decrease in the dispersity of oxides of Ce and Pd. The phase composition of the sample did not change, which is a clear evidence of a high thermal stability of this sample.

The data on the activity of the samples with different content of ceria, calcined at 1,000 °C (initial samples) and the activity of these samples after the treatment in the reaction mixture (1% of methane, balance air, at 1,000 h<sup>-1</sup> for 3-6 h) are given in Table 3.

As follows from the data in Table 3, all samples treated in the medium containing methane were activated, with the highest activation degrees achieved on the sample containing 12% of ceria. After the first treatment, the  $\Delta T$  value was -60 °C at the measurements with the increasing temperature in the reactor, and -100 °C

**Table 2. The effect of the support composition and the calcination temperature on the structural properties of catalysts containing 0.8% Pd**

#	Support composition	$S_{BET}$ , m <sup>2</sup> /g	Phase composition
Calcination temperature 600 °C			
1	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> "pure"	174	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>
2	2%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	169	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>
3	5%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	160	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub>
4	12%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	150	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub>
5	15%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	145	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub>
Calcination temperature 800 °C			
6	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> "pure"	122	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; PdO
7	2%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	128	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; PdO
8	5%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	142	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub> ; PdO
9	12%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	135	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub>
10	15%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	122	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub>
Calcination temperature 900 °C			
11	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> "pure"	101	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; $\delta$ -Al <sub>2</sub> O <sub>3</sub> ; PdO
12	2%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	100	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; $\delta$ -Al <sub>2</sub> O <sub>3</sub> ; PdO
13	5%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	110	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; $\delta$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub> ; PdO
14	12%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	90	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub> ; PdO
15	15%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	75	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub> ; PdO
Calcination temperature 1,000 °C			
16	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> "pure"	52	$\theta$ -Al <sub>2</sub> O <sub>3</sub> ; $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (~25%); PdO
17	2%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	70	$\theta$ -Al <sub>2</sub> O <sub>3</sub> ; $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (~1%); PdO
18	5%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	70	$\theta$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub> ; PdO
19	12%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	75	$\theta$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub> ; PdO
20	15%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	55	$\theta$ -Al <sub>2</sub> O <sub>3</sub> ; CeO <sub>2</sub> ; PdO

**Table 3. Data on the temperature of 50% methane conversion on ceria content in Pd-ceria-alumina catalysts**

#	Catalyst composition	T <sub>1</sub> , °C		T <sub>2</sub> , °C ( $\Delta T = T_2 - T_1$ )		T <sub>3</sub> , °C ( $\Delta T = T_3 - T_1$ )	
		T' <sub>50</sub>	T <sup>D</sup> <sub>50</sub>	T' <sub>50</sub>	T <sup>D</sup> <sub>50</sub>	T' <sub>50</sub>	T <sup>D</sup> <sub>50</sub>
1	0.8% Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	330	360	330 (0)	330(-30)		
2	0.8% Pd/2%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	360	380	360 (0)	370(-10)		
3	0.8% Pd/5%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	340	370	320 (-20)	320(-50)		
4	0.8% Pd/12%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	360	400	300 (-60)	300(-100)	260(-100)	260 (-140)
5	0.8% Pd/15%CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	330	400	325 (-5)	330(-70)		

T<sub>1</sub> is the temperature of 50% methane conversion of the fresh prepared catalyst calcined at 1,000 °C for 4 h; T<sub>2</sub> is the temperature of 50% methane conversion on samples after the catalyst 3 h treatment under the conditions T=800 °C, 1% CH<sub>4</sub>+air; GHSV=1,000 h<sup>-1</sup>, T<sub>3</sub> is the temperature of 50% methane conversion on samples after 6 h treatment under the conditions T=800 °C, 1% CH<sub>4</sub>+air; GHSV=1,000 h<sup>-1</sup>, T'<sub>50</sub> are obtained at increasing temperature in the reactor, T<sup>D</sup><sub>50</sub> are obtained at decreasing temperature in the reactor.

at the decreasing temperature. After the second treatment step, this effect was further increased, and the temperature of 50% methane conversion was decreased by 40 °C more in the both regimes.

Fresh prepared catalysts containing ceria calcined in air at 1,000 °C exhibit inferior catalyst activity to that of 0.8%Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> treated in the same way, and there is a difference between the upward and downward activity traces, which can be possibly explained by transformations of Pd active sites during temperature change.

It was shown previously that ceria increases the stability of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts due to its ability for oxygen storage and thus keeping Pd in the more active oxidized state-PdO. The presence of ceria also caused the hysteric behavior of catalytic activity to disappear [Deng and Nevel, 1999].

Study of Pd/ceria/alumina samples prepared in this work shows that this effect of hysteresis disappearance is observed only after the treatment of the catalysts at 800 °C in the reaction mixture—1% of methane in air—and this treatment also leads to the activation of catalysts containing 5-12 wt% ceria. Lyubovsky and Pfefferle, 1999 pointed out that the effective Pd surface area and the number of active sites is varying during the reaction at different reaction conditions. Probably, the treatment with the reaction mixture results in the better contact and interaction between Pd and ceria particles, resulting in a higher catalyst activity.

The results obtained allow drawing the conclusion about high thermal stability of Pd-ceria-alumina catalyst prepared on the base of alumina doped with 12 wt% of CeO<sub>2</sub> and containing 0.8% Pd. Thus, this catalyst formula can be recommended for further testing in processes of high temperature methane combustion.

## 2. Mn-Al-O Catalysts

A series of Mn containing oxide catalysts on spherical (1.4-1.8 mm)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub>, pure or doped with La, Ce and Mg oxides were prepared. The catalysts were characterized by chemical analysis, X-ray phase analysis, BET surface area and activity measurements in methane oxidation.

The characteristics of the catalysts are given in Table 4.

In the non-modified samples calcined at 900 °C, in addition to  $\delta$ -Al<sub>2</sub>O<sub>3</sub>, traces of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are detected. The formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at a temperature as low as 900 °C is explained by the manganese mineralizing effect on alumina.

In the Mg-containing sample calcined at 900 °C the perfecting of the solid solution and the increase of the crystal lattice parameter take place.

According to XRD data in the catalysts modified by lanthanum and calcined at 900 °C the lattice parameter corresponds to that of the initial support, independent on  $\chi$ -Al<sub>2</sub>O<sub>3</sub> content. In the catalysts modified by cerium, the change in the lattice parameter is also insignificant, and in all samples the CeO<sub>2</sub> phase is present.

In the case of support modified by magnesium, upon its additional modification by lanthanum or cerium, the same forming features of catalyst phase composition are preserved as in the case when the support is modified only by magnesium. For instance, at 900 °C the perfecting of mixed solid solutions structure takes place with the increase of lattice parameters, while the manganese oxide phases are absent in all the samples, which is associated with the formation of the solid solution of manganese cations in the structure of ( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub>. It should also be noted that at this temperature the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase is absent in all the La- and Ce-containing catalysts, as a result of the thermal stabilization effect of the named additives.

The results of the studies of the catalyst activity in the reaction of methane oxidation are shown in Fig. 2. It can be seen that the activity of the manganese catalysts based on the prepared supports  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub> is higher than that of the commercial manganese oxide catalyst. With this exception, the activities of cata-

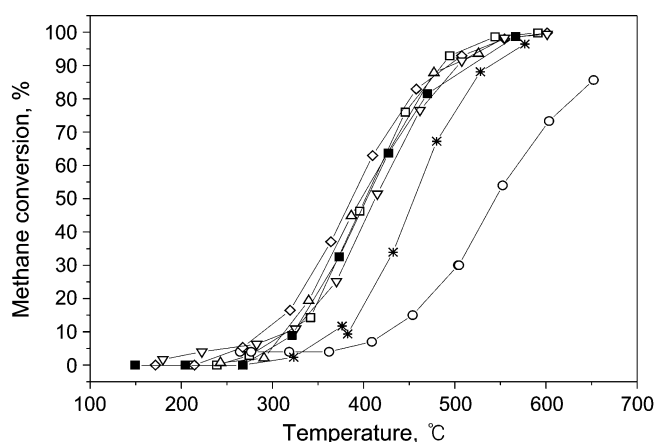


Fig. 2. Activity of Mn-Al-O catalysts in methane oxidation measured in a flow setup.

□ - 5%Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ◇ - 5%Mn/( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub>, ○ - 5%Mn/( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub> (Commercial), △ - 5%Mn/( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub>+MgO, ▽ - 5%Mn/( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub>+MgO+La<sub>2</sub>O<sub>3</sub>, \* - 5%Mn/( $\gamma$ + $\chi$ )-Al<sub>2</sub>O<sub>3</sub>+MgO+CeO<sub>2</sub>, ■ - 10%Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

Table 4. Composition and properties of Mn-Al-O spherical (1.4-1.8 mm) catalysts with Mn content (calculated as MnO<sub>2</sub>) equal to ~5%

#	Catalyst	Support composition	$S_{BET}$ , m <sup>2</sup> /g, 900 °C	XRD samples calcined at 900 °C
1	Mn-Al-O	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	115	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (~1%) ( $\delta$ + $\gamma^*$ )-Al <sub>2</sub> O <sub>3</sub>
2	Mn-La-Al-O	La/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	115	$\gamma^*$ -Al <sub>2</sub> O <sub>3</sub> (a~7.915 Å)
3	Mn-Ce-Al-O	Ce/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	110	$\gamma^*$ -Al <sub>2</sub> O <sub>3</sub> +CeO <sub>2</sub> (a~7.912 Å)
4	Mn-Al-O	(75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +25% $\chi$ -Al <sub>2</sub> O <sub>3</sub> )	130	$\beta$ -Mn <sub>2</sub> O <sub>3</sub> + $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (~2%)+( $\delta$ + $\gamma^*$ )-Al <sub>2</sub> O <sub>3</sub>
5	Mn-La-Al-O	La/(75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +25% $\chi$ -Al <sub>2</sub> O <sub>3</sub> )	107	$\gamma^*$ -Al <sub>2</sub> O <sub>3</sub> (a~7.917 Å)
6	Mn-Ce-Al-O	Ce/(75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +25% $\chi$ -Al <sub>2</sub> O <sub>3</sub> )	121	$\gamma^*$ -Al <sub>2</sub> O <sub>3</sub> +CeO <sub>2</sub> (a~7.918 Å)
7	Mn-Mg-Al-O	Mg/(75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +25% $\chi$ -Al <sub>2</sub> O <sub>3</sub> )	108	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (traces)+ $\gamma^*$ -Al <sub>2</sub> O <sub>3</sub> (a~7.965 Å)
8	Mn-Mg-La-Al-O	La+Mg/(75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +25% $\chi$ -Al <sub>2</sub> O <sub>3</sub> )	114	$\gamma^*$ -Al <sub>2</sub> O <sub>3</sub> (a~7.956 Å)
9	Mn-Mg-Ce-Al-O	Ce+Mg/(75% $\gamma$ -Al <sub>2</sub> O <sub>3</sub> +25% $\chi$ -Al <sub>2</sub> O <sub>3</sub> )	111	CeO <sub>2</sub> + $\gamma^*$ -Al <sub>2</sub> O <sub>3</sub> (a~7.956 Å)

$\gamma^*$ -Al<sub>2</sub>O<sub>3</sub> is solid solution based on the spinel structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a lattice parameter shown.

**Table 5. The results of activity tests in the reaction of methane oxidation in the presence and the absence of water vapor (20 vol%) in the initial reaction mixture**

Catalyst	$T_{50\%}, ^\circ\text{C}$	
	No $\text{H}_2\text{O}$ added	20% $\text{H}_2\text{O}$
5% Mn/ $\gamma\text{-Al}_2\text{O}_3$	400	480
5% Mn/(( $\gamma$ + $\chi$ )- $\text{Al}_2\text{O}_3$ )	400	450
5% Mn/(( $\gamma$ + $\chi$ )- $\text{Al}_2\text{O}_3$ +Mg)	400	440
5% Mn/(( $\gamma$ + $\chi$ )- $\text{Al}_2\text{O}_3$ +Mg+Ce)	450	510
5% Mn/(( $\gamma$ + $\chi$ )- $\text{Al}_2\text{O}_3$ +Mg+La)	410	490
10% Mn/ $\gamma\text{-Al}_2\text{O}_3$	400	450

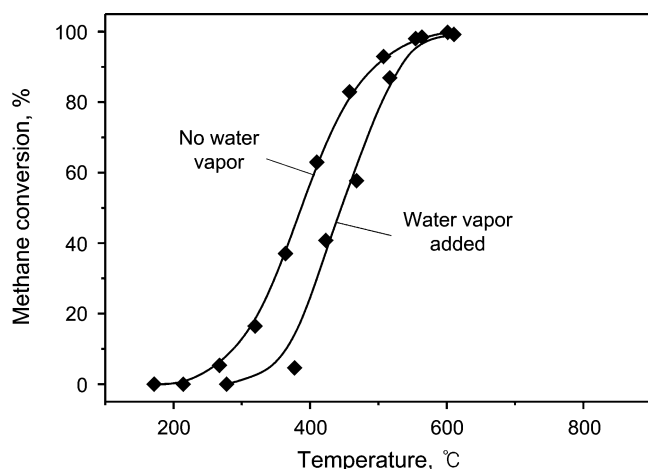
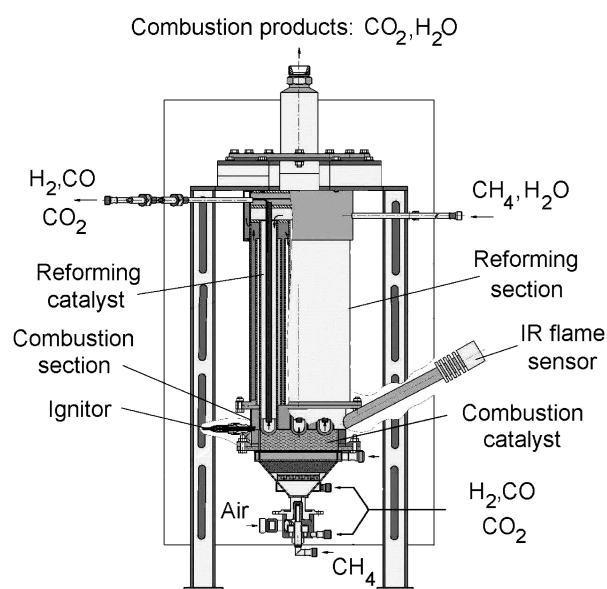
lysts with the equal manganese content, both on the modified and non-modified supports, are close to each other. The increase of Mn content from 5 to 10% does not affect the catalyst activity.

The temperatures for methane 50% conversion are about  $400^\circ\text{C}$  for the majority of Mn catalysts studied, which is not much higher than the temperatures for methane 50% conversion observed on palladium-ceria catalysts ( $350\pm 50^\circ\text{C}$ , Table 3).

At the same time, the presence of thermal stabilization additives of La and Ce in Mn catalysts is expected to provide durability of Mn-Al-O catalysts at temperatures higher than  $1,000^\circ\text{C}$ .

As the exhaust anode gas fed to the catalytic burner can contain significant amounts of water vapor (up to 20 vol%) in addition to CO,  $\text{H}_2$  and  $\text{CH}_4$ , it was important to study the effect of the water presence in the initial mixture on the catalyst performance.

The presence of 20% water in the initial mixture, as a rule, increases the temperature of 50% methane conversion by  $40\text{--}80^\circ\text{C}$  (Table 5, Fig. 3). However, as it is shown by the typical shape of the temperature dependencies of  $\text{CH}_4$  conversion (Fig. 3), the inhibiting influence of water is noticeable at  $250\text{--}550^\circ\text{C}$ , while at temperatures above  $550^\circ\text{C}$  the presence of water does not influence the completeness of methane oxidation. Similar temperature dependence of the effect of water vapor on methane combustion was found for Pd supported on alumina doped by zirconia [Ciaparu and Pfefferle, 2001]. This can be explained by water adsorption on the cat-

**Fig. 3. Effect of addition of 20 vol% of water vapor on efficiency of  $\text{CH}_4$  oxidation over Mn-Al-O catalyst (#4 in Table 4).****Fig. 4. The drawing of the pilot catalytic reformer with a catalytic burner.**

alyst surface, blocking the active sites at lower temperatures. At higher temperatures the concentration of adsorbed water decreases and this effect disappears.

The experiments have shown that by depositing manganese oxide on the modified alumina it is possible to obtain the aluminum-manganese oxide catalyst, surpassing existing industrial analogues by activity and thermal stability at high temperatures - up to  $1,000\text{--}1,300^\circ\text{C}$  [Tsykosa et al., 2001]. The high thermal stability of these catalysts can be explained by the formation of solid solutions at  $900^\circ\text{C}$  or hexaaluminates at  $1,300^\circ\text{C}$  due to interaction of manganese oxide with the catalyst support.

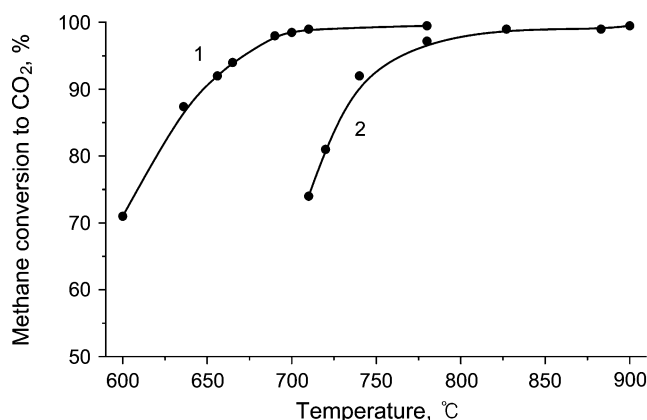
### 3. Design of a Model Reformer with a Catalytic Burner

A model reformer for methane steam reforming was designed and fabricated for testing in the composition of the bench-scale Fuel Cell Power Plant (Fig. 4). The reformer is designed in two modifications: the one with a flame diffusive burner, and the other with a catalytic burner. The burners are made replaceable for possibility to make the comparative analysis of the results that will allow the evaluation of the advantages of the catalytic burner.

The reformer with the catalytic burner contains a catalytic reforming unit in the heat insulated casing with a burner located below. The reformer section consists of seven tubular modules containing Ni/ $\text{Al}_2\text{O}_3$  catalyst for methane reforming. Each module consists of three concentric tubes. The outer tube serves for the passage of the hot combustion gases that heat the catalyst in the middle tube, the middle tube contains the granulated catalyst for methane reforming, and the inner tube serves for the outlet of the hydrogen containing gas formed over the catalyst.

The catalytic burner contains combined mixer, conical diffuser, porous and granular gas distributors and catalytic bed that can be filled either by granular or structured (monolithic or foam) catalysts. Above the bed an electric igniter and a photoelectric flame detector are situated.

The preliminary testing of the model reformer showed that the parameters of the catalytic reformer operation and the composition



**Fig. 5. Methane conversion vs temperature in a laboratory catalytic burner: on the commercial catalyst IC-12-73 (Cu-Mg  $\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ ) (1) and Mn-Al-O catalyst modified with La and Mg (2).**

Conditions: catalyst loading 150 g, GHSV=2,800  $\text{h}^{-1}$ ,  $\text{CH}_4$  conc. 4.4-6.5%; air excess coefficient  $\alpha=2.3$ -1.5

of the hydrogen-enriched gas are close to the theoretical values. The temperature in the reformer was stabilized at the optimum of 785 °C.

A batch of Mn-Mg-La-Al-O catalyst was prepared for further testing in a model reformer with a catalytic burner.

Preliminary tests of Mn-Mg-La-Al-O in a laboratory catalytic burner in comparison with a commercial combustion catalyst are shown in Fig. 5. It can be seen that at low temperatures the commercial combustion catalyst exhibit superior performance; however, the operation of this catalyst is limited to temperatures below 800 °C. The Mn-Al-O catalyst provides efficient methane combustion at temperatures above 750 °C and can be used at rather high temperatures: up to 1,100-1,300 °C.

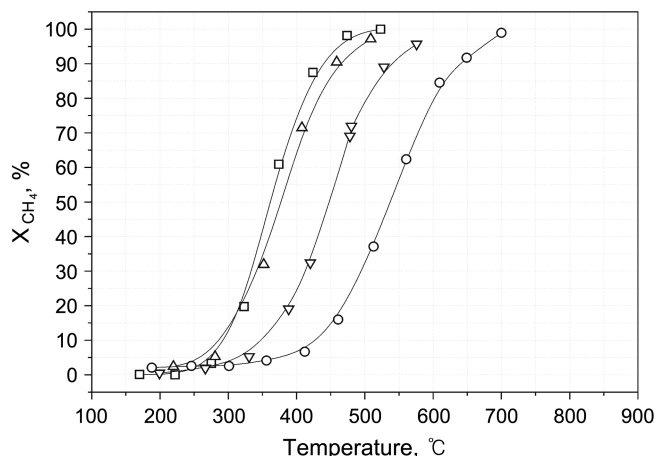
The results of the experiments carried out in the prototype catalytic burner designed and constructed for catalyst testing in the

composition of the bench-scale Fuel Cell Power Plant are shown in Table 6. The catalysts were tested under realistic conditions at high temperatures and at methane concentrations close to stoichiometric values.

Under these conditions the Mn-Al-O catalysts provide complete methane combustion at near-stoichiometric mixtures with air (Table 6).

After experiments that lasted for 23 hours, samples of catalysts were taken from the different locations of the bed for catalyst activity studies.

The measurement of the activity of the commercial IC-12-73 cat-



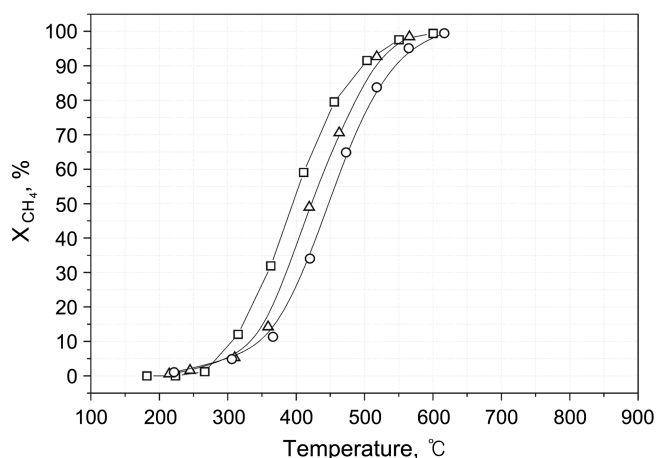
**Fig. 6. Catalytic activity in the reaction of methane oxidation of IC-12-73 catalyst samples after testing the catalyst in the prototype catalytic burner for 23 hours, taken from different parts of the catalyst bed with different operation temperatures.**

□ - IC-12-73, initial; △ - sample from top (532 °C); ▽ - sample from middle (997 °C); ○ - sample from bottom (1,205 °C)

**Table 6. The results of testing the pilot burner with Mn-Mg-La-Al-O catalyst: catalyst loading 220  $\text{cm}^3$ , air feed rate 0.5-0.55  $\text{nm}^3/\text{h}$ , methane feed rate 0.05  $\text{nm}^3/\text{h}$ ,  $\alpha=1.0$ -1.16; GHSV=2,400-2,700  $\text{h}^{-1}$**

Experimental conditions			Composition of the reaction products, vol% in dry gas				
$\alpha^*$	$T_1$	$T_2$	$\text{H}_2$	$\text{CO}$	$\text{CH}_4$	$\text{CO}_2$	$\text{O}_2$
1.00	1204	1002	0.0100	0.0017	0.0090	11.46	0.06
1.05	1217	1013	0	0.0077	0.0047	10.37	1.03
1.06	1199	987	0	0.0069	0	10.12	1.24
1.07	1142	996	0	0.0062	0.0084	10.19	1.34
1.07	1194	998	0	0.0074	0	10.10	1.44
1.08	1187	1007	0	0.0064	0.0029	10.07	1.53
1.15	1135	1003	0	0	0	10.34	2.67
1.16	1134	1002	0	0	0	9.93	2.96

\* $\alpha$  is air excess coefficient defined as actual air supply rate divided by stoichiometric air supply rate;  $T_1$  is temperature at the lower part of the catalyst bed - 5 mm above the porous plate whereupon the catalyst is loaded;  $T_2$  is temperature in the middle of the catalyst bed - 25 mm above the porous plate whereupon the catalyst is loaded.



**Fig. 7. Catalytic activity in the reaction of methane oxidation of Mn-Mg-Al-O catalyst before and after testing the catalyst in the prototype catalytic burner for 23 hours, taken from different parts of the catalyst bed with different temperatures.**

□ - Mn-Mg-Al-O initial; △ - sample from top (708 °C); ○ - sample from bottom (1,103 °C)

alyst samples showed that at long catalyst operation (>20 h) a sharp decrease in the activity of the samples taken from the lower high-temperature part of the catalyst bed ( $T_{50\%}=550^\circ\text{C}$ ) takes place (Fig. 6).

The catalyst Mn-Mg-Al-O proved to be more stable in comparison with IC-12-73 catalyst. The catalyst operation at temperatures exceeding 1,100-1,200  $^\circ\text{C}$  leads to the increase of  $T_{50\%}$  by 50  $^\circ\text{C}$ , on the average, resulting in  $T_{50\%}=450^\circ\text{C}$  (Fig. 7).

Thus, the results obtained show that IC-12-73 catalyst has a high initial activity. At the same time the operation of this catalyst at high temperatures leads to considerable decrease in the catalytic activity ( $T_{50\%}$  increase by 200  $^\circ\text{C}$ ).

On the contrary, the activity of the manganese catalysts does not decrease much. The temperature for attaining 50% methane conversion for this catalyst increases only by  $\sim 50^\circ\text{C}$ .

Therefore, this catalyst is chosen for further durability studies in the catalytic burner for combustion of methane and anode gas mixtures, as well as Pd-ceria catalyst of optimum composition containing 12 wt% ceria.

The long-term testing of Pd-ceria catalysts and Mn-Al-O catalysts will be the subject of another article.

## CONCLUSION

A series of spherical Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared for testing in the catalytic burners of fuel cell power plant reformers. An optimum concentration of ceria 12 wt% providing the highest thermal stability of catalysts was determined. The effect of catalyst activation in the reaction mixture containing methane was observed.

A series of Mn containing oxide catalysts on spherical  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or ( $\gamma$ - $\chi$ )-Al<sub>2</sub>O<sub>3</sub>, both pure and doped with La, Ce and Mg oxides were prepared. The catalysts were characterized by chemical analysis, X-ray phase analysis, BET surface area and activity measurements in methane oxidation.

A model reformer with a catalytic burner was designed and fabricated for testing in the composition of the bench-scale Fuel Cell Power Plant. A batch of Mn-Mg-La-Al-O catalyst was prepared for long-term testing in the model reformer with a catalytic burner. Preliminary testing of this catalyst in the burner for 23 h showed that it provides complete methane combustion and stable performance at realistic conditions in the burner with a catalyst bed temperature of 1,000-1,200  $^\circ\text{C}$ .

## ACKNOWLEDGMENTS

To the International Science and Technology Center for support of this work in frame of ISTC project # 16 78 and INTAS 99-1044.

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