

CATALYTIC FLAMELESS COMBUSTION OF FUELS - A PROMISING ECOLOGICALLY CLEAN METHOD FOR OBTAINING ENERGY AND ITS USE FOR NEUTRALIZATION OF TOXIC ORGANIC COMPOUNDS

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Abstract:

The catalytic flameless combustion of hydrocarbon fuels (methane, propane, butane, kerosene, etc.) is investigated over various block oxide catalysts of perovskite structure. The possibility to vary the temperature developing in the catalyst block in the wide range (800-1600°C) through the catalyst composition is shown. The transformations of various toxic organic compounds in methane flameless combustion are investigated. It is shown that various oxygen-, nitrogen-, halogen-containing organic compounds undergo transformation not forming any toxic products. We have the samples of catalysts with the same properties, which contain 2-10% Pt supported on Zr oxide and its compositions but their switch temperature is much less (80-100°C).

Key Words: *flameless combustion; perovskite; block oxide catalysts*

Introduction

The catalytic flameless combustion of hydrocarbon fuels (methane, propane, butane, kerosene, etc.) is investigated over various oxide catalysts. These catalysts allow complete combustion for the prolonged time periods and ecologically clean waste, therefore the process developed seems to be the good alternative to the usual fuel combustion in flame where the amount of released toxic components (NO_x, CO, organic compounds) is high. Recently, a considerable attention has been attracted to perovskites as catalysts of various high temperature processes due to their high activity, thermal stability and poison resistance^[1]. Within the current concept of the multiple bed design of combustion chambers (i.e. for gas turbine application)^[2], perovskites can be used in the middle section to support combustion of the air + fuel mixture ignited by more active supported Pd catalysts. For processes requiring a low pressure drop

across the catalyst bed, bulk or supported honeycomb monolithic perovskites seem to be promising. The performance of such catalysts depends on (i) the properties of the active component (its chemical composition, dispersion and defect structure), (ii) the chemical interaction between the active component and a support or binder used for the monolith shaping, (iii) the monolith pore structure. For catalytic combustion, the chemical and thermal stability of monolith catalysts in gas streams with a high content of water and carbon dioxide is also demanded.

Manganites, nickelates, ferrates and cobaltites of lanthanum and their solid solutions are usually considered as being among the most active compounds. It is worth mentioning that reliable data on the specific catalytic activity of perovskites tested as monoliths are nearly absent^[3].

For any practical wide-scale application, the price of catalyst has to be reasonably low. To meet this demand, simple, waste-

less and inexpensive method of perovskites synthesis via the mechanochemical activation of solid reagents appears to be attractive^[4]. To decrease expenses further, a mixture of commercially available lanthanides oxides containing mostly lanthanum and cerium or Dy-Y could be used. For some perovskites, such substitution of lanthanum for cerium is known to increase the catalytic activity.

Monolithic corundum-supported perovskites are also worth considering as a choice for the practical application provided their catalytic activity is not suppressed due to interaction of the active component with support.

In this paper, the results on the catalytic activity in methane combustion of Ln-Me-O mixed oxides (Ln = La+ Ce, Dy+Y ; Me= Mn, Ni, Fe) synthesized via the route of solid precursors mechanical activation and shaped as monoliths using a boehmite - based binder modified by Ce or Zr oxides are presented. Methane is chosen here as being among alkanes the compound with the strongest C-H bond hard to be activated. Besides, methane is the main component of the natural gas used in the large-scale energy production. Isothermal experiments in controlled conditions were used to elucidate the effect on activity of such catalysts characteristics as their chemical composition, microstructure, pore structure, thermal stability, shape of monoliths etc. Catalytic properties of bulk and corundum-supported monolithic perovskite catalysts were compared with those of supported Pt and Pd catalysts. The best monolithic perovskites catalysts were tested in the autothermal mode of gas fuels combustion using a pilot installation.

Experimental

As starting compounds for synthesis, commercially available transition metal oxides and commercially available La-Ce or Dy-Y oxide solid solutions were used.

The monolith catalysts were prepared by kneading a powdered active component with pseudoboehmite (binder 1, produced by the «CATALYSATOR» company, Novosibirsk, specific surface area 200-250 m²/g) in the acid media (as peptizing agent, the nitric acid was used) and extruding the plastic paste through the proprietary die.

As supports for perovskites and Pt/Pd catalysts, proprietary corundum monoliths developed in BIC with wall thickness 0.25 mm and channel sizes ca 1 mm with specific surface area in the range of 5-10 m²/g annealed at 1300°C were mainly used. To suppress reactivity of alumina, a mullite surface layer was formed using impregna-

tion of support with silica sol followed by drying and high-temperature calcination

Perovskites were supported onto corundum micromonoliths with loadings up to 20 wt.% using nitrate salts and Pechini method^[5].

Pt (0.6wt. %) and Pd (0.2 wt. %) were supported onto monolithic supports or supported perovskites using impregnation by H₂PtCl₆ and PdCl₂ solutions, respectively, by the incipient wetness method followed by drying and calcination at 700°C.

The methane oxidation activity of all the catalysts was measured at the atmospheric pressure in the tubular integral plug-flow reactors with 8 mm and 25 mm i. d. fed by the gas mixture containing 0.5-1 % CH₄ and 2-20 % O₂ in He (N₂). The reactor was loaded either with the 0.5-1 mm particles of catalyst packed as a layer between the quartz wool plugs, or with a piece of monolith. The inlet and outlet gas concentrations were analysed by GC. The temperature was varied from 300°C to 700-900°C starting from keeping the catalyst in the reaction mixture for 2 h at the highest temperature. Unless otherwise stated, a relative contact time τ defined as a ratio of the reactor volume occupied by the layer of catalyst or a piece of monolith (cm³) divided by the flow rate (cm³/s) was used for the data analysis. Space velocity was varied in the range of 2,000-60,000/h.

The autothermal flameless combustion of fuels was studied in the pilot installation comprised of 45 mm diameter quartz tube equipped with the methane burner to preheat the monolithic catalyst. This burner ensures also the air and fuel mixing and supply to monolithic catalyst during the flameless combustion. Typically, a piece of monolith with a volume ca 150 cm³ is fixed into the reactor, and thermocouple is inserted in the central channel at the middle of monolith. The thermal insulation of monolith from the reactor walls is made by wrapping it in a piece of a ceramic fiber cloth. To ignite the process of combustion, the monolith is heated by the flame burner up to 300-500°C as dependent upon the type of fuel and properties of monolithic catalyst. After that the flame is extinguished, and the fuel+ air mixture is fed to the monolithic catalyst at the fuel: air ratio ~ 1:8-1:10 and space velocities up to 25,000/h. Due to the flameless combustion of fuel, the steady-state catalyst temperature is increased up to 1000-1200 °C. To change the fuel composition and/or to introduce the typical catalytic poisons into the feed, the air is passed through the saturator filled with various organic substances (benzene etc) and kept at desired temperatures. The inlet and outlet gas mixtures com-

position was analyzed using a Tesla-33 electrochemical analyzer along with a photo-acoustic GAPA analyzer.

Results

Table 1 lists typical data on the chemical composition, specific surface area and the integral pore volume for some samples studied here.

The most extensive pilot testing was carried out for bulk monolithic lanthanum

manganite catalyst due to its good performance and the best ability to keep the process of the fuels flameless combustion in the autothermal mode. Some typical results are presented in Table 2. As follows from these data, the level of NO_x emission is very low. Similar results not shown here for brevity were also obtained with such fuels as propane-butane and kerosine. As analogs of more heavy fuels, benzene and toluene were introduced into the air+methane feed (Table 3).

Table 1. The chemical composition, integral pore volume, specific surface area and some kinetic data for catalysts.

No	Oxide system + binder	S, m ² /g (BET)	S _p , m ² /g (Hg)	V _p , cm ³ /g (Hg)	E _a , kcal/mol	K ₅₅₀ , 10 ⁻² s ⁻¹ m ⁻²
1	Ln-Mn-O + Al ₂ O ₃	25	17	0.25	21.2	1.12
2	Ln-Mn-O + Al ₂ O ₃ + Ce+La	9.7	9.7	0.186	21.5	2.57
3	Ln-Mn-O + Al ₂ O ₃ + Ce+La+Ni	14	9.4	0.196	20.7	2.94
4	Ln-Fe-O + Al ₂ O ₃ + Ce+La +Ni	16	10.9	0.16	25.4	1.4
5	Ln-Ni-O + Al ₂ O ₃ +Ce+La +Ni	19	16.8	0.14	28.8	1.5
6	Ln-Mn-O +Al ₂ O ₃ +Ce+La +Co	12	12.2	0.182	21.8	2.85
7	Ln-Fe-O +Al ₂ O ₃ +Ce+La +Co	16	17	0.16	26.0	1.57
8	Ln-Ni-O +Al ₂ O ₃ +Ce+La +Co	21	18.7	0.142	26.8	1.15
9	Ln-Mn-O +Al ₂ O ₃ + Ce+La +Ni +coarse particles	28			23.5	1.8
10*	LnMnO ₃ + Al ₂ O ₃ +Ce+La +Ni + coarse particles + fibers	23 (1.3)			23.3 (22.4)	2.85 (1.3)
11*	Ln-Mn-O, Al ₂ O ₃ + particles + fibers	55 (0.2)			23 (18.9)	2.66 (11)

* Data after calcinations at 1100 °C are given in parenthesis

Table 2. Catalytic flameless combustion process parameters on La-Mn monolith catalysts of perovskite type. Autothermal mode, space velocity 25000 h⁻¹

Methane: Air ratio	Monolith temperature, °C	Some exhaust components		
		NO _x , ppm	CO, %	CH ₄ , %
1:8	950	1-3	0.72	0.3
	960	1-3	0.62	0.3
	960	1-3	0.45	0.3
1:9	970	1-3	traces	0.06
	920	1-3	traces	0.08
	880	1-3	0.0	0.11
1:10	910	1-3	0.45	0.5
	910	1-3	0.45	0.6
	910	1-3	0.40	0.5

Table 3. Conversion of different organic compounds in the methane flameless combustion process (methane/air flow with 1:8 ratio and space rate 11000 h^{-1} was saturated by organic admixture at $25 \text{ }^\circ\text{C}$).

Organic compound	Boiling point, $^\circ\text{C}$	Conversion of added compound, %	NO_x content in the combustion products, ppm
Benzene	80.1	98	0
Toluene	110.6	99	0
Acetone	56.0	99.9	0
Diethyl ether	34.5	99	0
Mixture of n-hexanol-45% and n-hexylamine-55%	100.0	100	40
Chloroform	61.2	84	

Prolonged testing of perovskite monoliths in the reaction of methane flameless combustion at 1173 -1373 K (for two months with daily start-up and shut-down) revealed no loss of activity and monolith integrity.

Discussion

Bulk monolithic perovskites

For all samples, the variation of the relative contact time and analysis of corresponding conversions in the range of 10-60 % have revealed that the rate of methane oxidation is rather well described by the equation with the first order in methane and zero orders in oxygen and carbon dioxide. The values of the first-order reaction rate constants calculated for the catalysts fractions and normalized to the surface area are included in Table I along with the activation energies estimated from their temperature dependence in the range of $300\text{-}500^\circ\text{C}$. High values of activation energies obtained here imply the absence of the internal diffusion limitations, that agrees with the absence of any apparent correlation between the specific rate constant and the integral pore volume. Indeed, at temperatures up to 500°C , the reaction rate constants normalized to the weight unit were found to be identical for the case of catalysts tested both as monolithic pieces and a layer of the catalyst fraction .

Supported monolithic catalysts

Supported perovskites are somewhat less active as compared with the bulk samples, probably, due to a rather well developed pore structure of the latter which ensures an easy access of reagents into the bulk monolith walls. However, their performance and thermal stability are rather good being comparable with those of supported Pt catalysts. Moreover, their activity is greatly improved, clearly in a non-additive manner, by a small amount of Pt. Hence, these sys-

tems are also deserving attention for the practical application.

Pilot testing

As follows from results presented in Table 2, 3, their flameless combustion proceeds also very efficiently without emission of NO_x . As an example of nitrogen-containing fuels, the mixture of hexanol and hexylamin was added to the feed. Even in this case, emission of nitrogen oxides was reasonably low. Such typical Cl-containing catalytic poison as chloroform was also efficiently combusted without deteriorating the catalyst performance.

At present, among monolithic catalysts with the oxidic-type active component, our catalysts are unique in their ability to support the flameless fuels combustion in the auto-thermal regime, which was earlier known to be accessible only for supported precious metal catalysts.

Conclusions

Low cost and active bulk and supported perovskite monolith catalysts for fuels flameless combustion were developed. For mixed oxide composites with perovskite -or fluorite-like structures bound with alumina, the specific catalytic activity in methane oxidation weakly depends upon the nature of transition metal cations (Mn, Ni, Fe, Co) being mainly determined by the binder composition and preparation procedure. These catalysts have a sufficient thermal stability at temperatures up to 1000°C , that makes them suitable for practical application in the flameless gas fuels combustion for the energy production.

References

- [1] Yamazoe and J. Teraoka, *Cat. Today*, 8 (1990) 175.
- [2] M. F. M. Zwinkels, S.G.Jaras, P.G. Menon and T. A. Griffin, *Catal. Rev.-Sci.*, 35 (1993) 319.
- [3] P. Ciambelli, V. Palma, S. F. Tikhov, V. A. Sadykov, L. A. Isupova, L. Lisi, *Catal. Today* 47 (1999) 199
- [4] L. A. Isupova, V. A. Sadykov, L. P. Soloviova, M. A. Andrianova, V. P. Ivanov, G. N. Kryukova, V. N. Kolomiichuk, E.G. Avvakumov, I. A. Pauli, O. I. Andryushkova, V. A. Poluboyarov, A. Ya. Rozovskii and V. F. Tretyakov, in G. Poncelet, J. Martevs, B. Delmon, P.A. Jacobs and P.G. Range (Editors), *Preparation of Catalysts VI. Sci. Bases for the Preparation of Heterogeneous Catalysts*, Proc. of the 6th Int. Symp. Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la Neuve, Belgium, 5-8 September 1994, Elsevier Science, Amsterdam, 1995, p. 637
- [5] M. P. Pechini, US Patent 3,330,697 (1967).