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Monolith perovskite catalysts for environmentally benign fuels combustion and toxic wastes incineration

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Abstract

Monolith perovskite catalysts for high-temperature applications (fuels combustion, toxic wastes incineration, hydrocarbons reforming, sulfur dioxide reduction, etc.) were elaborated. Basic stages of these catalysts manufacturing (synthesis of perovskites ultradispersed powders via effective wasteless plasmochemical and mechanochemical routes, monoliths shaping by extrusion with subsequent drying and calcination) were developed. Pilot testing in a number of high-temperature catalytic processes demonstrated efficiency, thermal stability and thermal shock resistance of monolithic perovskites.

Keywords: Monolith perovskite catalysts; Environmentally benign fuels combustion; Toxic wastes incineration; Combustion

1. Introduction

Mixed oxides of transition and rare-earth metals possessing perovskite structure appear to be suitable for such high-temperature processes as catalytic combustion, methane reforming, ammonia oxidation, sulfur dioxide reduction, etc. due to their well-known thermal stability in a broad range of oxygen partial pressures and resistance to catalytic poisons [1,2].

Up to the present, catalytic properties of pure bulk perovskites or supported perovskites were mainly studied and reported [3–5]. Supported systems are rather limited by the content of the active component, and chemical interaction between active component and support at enhanced temperatures often causes loss of activity and mechanical strength. At the same time, bulk catalysts with homogeneous distribution of the structural additives and/or promoters are known to be the most thermally stable under real high-temperature conditions. Moreover, catalysts with high content of the active component are more resistant to such catalytic poisons as Cl, F, S-containing compounds. To minimize pressure drop across the catalytic bed, especially for gas streams with high linear velocities, honeycomb monoliths are required.

To elaborate the technology of perovskite monolith honeycomb catalysts production, the methods of preparation of highly dispersed, chemically active powders with uniform phase composition

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and narrow particle size distribution should be invented. Two techniques: mechanochemical activation (MA) of solid starting compounds in high powered ball mills with a subsequent thermal treatment [6,7] and arc plasma thermolysis (APT) of the mixed solutions of rare-earth and transition metals nitrates match these requirements [8].

The work presented was undertaken to develop new methods of active powdered perovskites preparation, to shape monoliths by extrusion and to investigate their catalytic properties.

2. Methods of the samples preparation and investigation

As starting compounds, oxides, carbonates (for MA synthesis) and nitrates (for APT synthesis) of lanthanum and transition metals were used. Mechanical activation of the starting compounds was carried out using high-powered planetary ball mills with an acceleration of ca. 40–60 g and milling balls to a powder weight ratio of ca. 10:1 [6,7,9]. After mechanical treatment the powders were annealed for 2–4 h at 700°C. Plasmochemical synthesis of perovskites was carried out in specially designed reactors equipped with 1–3 arc plasmatrons generating a flux of air plasma with an initial temperature in the range of 4–6 thousands of K. Mixed nitrites solutions were injected into the reaction zone via spray nozzles. The most efficient regimes were found to have current densities of ca. 40–60 A and the total supply of solution ranging from 1.5 to 3.0 g/s, concentration being ca. 10–15 wt-.% as calculated on MeO_x. Powders were separated from a gas flow by using cloth bag filters [8,9]. The catalysts of simple (cylinders) or complex (rings, honeycomb monoliths) forms were prepared by extrusion of the plastic pastes composed of perovskite powders with addition of binders, acid peptizers and some surfactants. After drying, monoliths were calcined at 500–1100°C for 2–4 h. Specific surface of the samples was determined by the BET method using Ar thermal desorption data. The aggregates size distribution was investigated by the Coulter method using a TA-2 machine and a DAS computer program [10]. Before measurements, powders were ultrasonically dispersed in the 1% NaCl solution. Phase composition was analyzed with a URD-63 diffractometer using CuKα radiation (scanning region was $2\theta = 4$–$30°$). X-Ray microprobe analysis (X-ray beam diameter ca. 2 μ) was carried out on a MAR-3 machine [11]. IR-spectra were recorded on a IR-75 spectrometer. The pore size distribution was investigated by the method of mercury porometry using an Auto-Pore 9200 machine. Transmission electron microscopic data (TEM) were obtained using a JEM-400C machine. The surface concentrations of the elements were determined by the SIMS method using a MC-7201 mass-spectrometer.

Catalytic activities in reactions of CO and butane oxidation in the excess of air were determined in the batch-flow systems equipped with the gas chromatographical analysis of the reaction mixture components, while activities in the reactions of methane steam (or carbon dioxide) reforming, sulphur dioxide reduction and ammonia oxidation were determined in fixed-bed flow systems (gas mixtures compositions and space velocities are given in the corresponding figures captions).

3. Results and discussion

3.1. Physical and chemical properties of perovskite powders

To elaborate perovskites synthesis via mechanochemical route, extensive studies of the effect of starting solids, types of mills and regimes of subsequent annealing on the degree of conversion into perovskites have been carried out [6,7].

The general feature of the solid-state reaction between activated phases was found to be a considerable influence of the stoichiometry of transition metal oxides. Thus, all other parameters being the same, nearly 100% conversion into per-

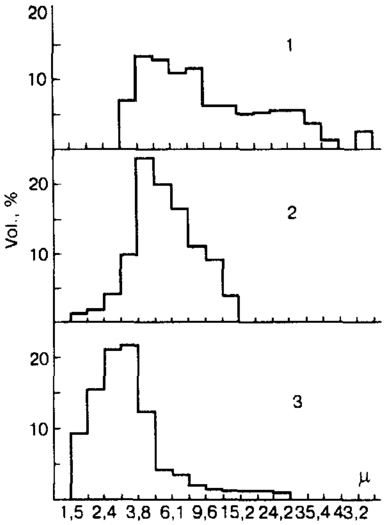

Fig. 1. Aggregates size distribution in $LaMnO_3$ powders obtained via: (1) MA, (2) ceramic, (3) APT routes.

ovskite was achieved with Co_3O_4 as a starting phase, while only 50% of CoO was converted into product. In a similar way, MnO_2 was found to be the most reactive between all the manganese oxides. MA allowed to decrease the temperature of the efficient solid-state interaction from 1100°C to 600–800°C, while duration of the reaction was reduced to several h from hundreds of h typical to ceramic technology [6,7]. No further calcination to obtain phase-pure perovskites is required when APT of mixed solutions is utilized. The perovskite powders thus obtained have rather high specific surface values (10–20 m^2/g), while ceramic route yields perovskites with $S_{sp} < 1$ m^2/g. As a rule, highly dispersed oxide powders are aggregated, and the size distribution of these aggregates may affect moulding properties as well as pore structure of the catalysts. In the case of perovskite powder aggregation also occurs (Fig. 1). This effect being especially well exhibited for the MA sample.

Perovskite prepared via APT and MA routes were also found to have higher specific activities than those obtained by ceramic or precipitation techniques [6,8]. Enhanced specific activity of lanthanum cobaltite prepared via mechanochemical route seems to be caused by some surface Co segregation. The latter effect was evidenced by SIMS and it rather good correlates with TEM data revealing surface clusters of CoO_x with typical dimensions of ca. 40–50 Å. Simultaneously, for this sample the XSAS method found an increased number of the regions with somewhat changed electron density [7,9].

In the case of lanthanum manganite prepared by plasmochemical method, an enhanced activity could be explained neither by phase composition nor by surface segregation of Mn [8]. According to TEM data, the particles of this sample have a nearly spherical form and possess a microdomain structure with nearly coherent stacking at the domain boundaries. Data of the X-ray methods which are also in favor of a high degree of this sample disordering are under preparation and will be published elsewhere.

Hence, in complex oxides with perovskite structure a disordering caused by strongly nonequilibrium conditions of synthesis is capable to increase low-temperature catalytic activity.

However, extended lattice defects generation can be achieved also by introduction of some cations capable to cause phase transition in perovskites. Thus, in the $La_{1-x}Sr_xCoO_3$ system at $x = 0.3$–0.4 a change of the structure symmetry from hexagonal to cubic occurs [12]. Namely these transient samples have the highest activity in CO oxidation correlating with the number of regions with somewhat changed electron density (integral density of extended defects) caused by a microdomain structure of the particles (Fig. 2).

Hence, for the first time a real structure of perovskites was shown to be important for low-temperature catalysis. Namely variation in defect structure of the samples with identical composition but prepared via different routes seems to explain structure sensitivity for the low-temperature (up to 200–300°C) oxidation reactions found in Ref. [13].

High-temperature (> 1100°C) perovskites sintering causes defects annealing that levels off activities of the samples prepared via different routes. However, enhanced initial reactivity of the disordered perovskite surfaces along with high dispersion is vital for ensuring good rheological

Fig. 2. Typical image of the $La_{0.6}Sr_{0.4}CoO_3$ particles [9], × 1 800 000.

properties of the plastic pastes to form monoliths by extrusion.

3.2. *Monolith shaping*

The basic approaches to the problem of obtaining plastic pastes with good rheology for shaping high-strength porous ceramics were developed by Rebinder [14] and Sczukin [15]. Such factors as high degree of powders dispersion (small particles sizes); enhanced reactivity of particles surfaces with respect to water, binders, acid addition, etc. are the most important. For the systems studied, high dispersion of perovskites prepared via APT is accompanied by an abundant hydroxilation of the surface layer together with the retention of the residual NO_3-groups as revealed by IR (Fig. 3). As a result, plasmochemical perovskites form water-based plastic pastes without any binder or electrolyte addition that allows to obtain high-strength extrudates even after 500°C calcination. Mechanical strength was found to be in direct proportion to the nitrates IR bands intensity. Thus, extrudates mechanical strength decreases in the order $LaCoO_3 > La_2CuO_4 > LaMnO_3$ correlating with the intensity of nitrates absorption bands (Fig. 3, 1040 cm^{-1} (ν_1), 825 cm^{-1} (ν_2), 1200–1600 cm^{-1} (ν_3), 720 cm^{-1} (ν_4) and hydroxiles (Fig. 3; absorption bands in the 3200–3600 cm^{-1} region) [16]. This trend means that bonding strength of each interparticle contact depends upon the surface density of the acid groups and hydroxiles. In a similar way, MA-powders calcined at 500–700°C can also be shaped as extrudates using pure water-perovskite pastes of an optimum humidity despite of the somewhat larger aggregates sizes. However, for these systems a reasonable level of the mechanical strength is attained only after calcination at 1000°C. These features of MA perovskites evidence that their somewhat decreased chemical reactivity is com-

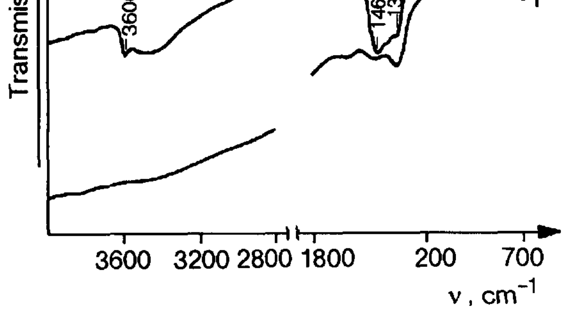

Fig. 3. IR-spectra of APT perovskite powders: (1) $LaMnO_3$, (2) La_2CuO_4, (3) $LaCoO_3$.

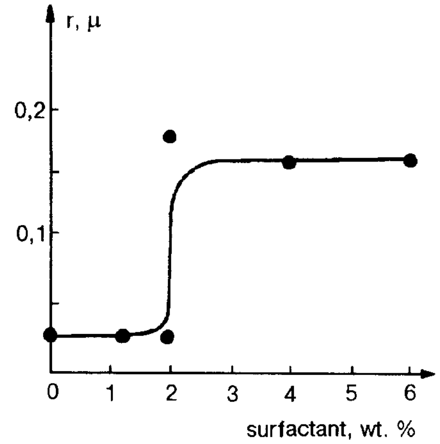

Fig. 4. Mean pore radius versus surfactant (ethylene glycol) content for monolithic $LaMnO_3$ (MA perovskite).

pared with the APT samples due to both absence of the residual nitrates and a lower degree of surface hydroxilation proved by IR-spectroscopy data. Despite of the smaller aggregates sizes, ceramic perovskites annealed at 1100°C do not form water-based plastic pastes (powders separation occurs). Here the key factor appears to be a low degree of surface hydroxilation (no bands of hydroxiles were detected). These data suggest that the ability of perovskite powders to form binder-free plastic pastes crucially depends upon the particles surface reactivity.

Enhanced reactivity of the APT and MA perovskites particles due to their high dispersion and structure disordering allows to shape not only simple extrudates but also rings provided optimum pastes humidity. To form perovskites as monoliths possessing high activity and good thermal shock resistance, optimization of the rheological properties of pastes, regimes of drying in controlled humidity conditions and calcination was carried out [7].

Pseudoboemite was found to be the most suitable binder ensuring high thermal shock resistance. Acetic and nitric acids were added for peptizing. When using nitric acid, more strong extrudates were obtained though integral pore volume and mean pore radius were also increased [7]. This means that strength of the interparticle contact is higher for the case of nitric acid addition. However, emission of nitrogen oxides at calcination stage makes this acid less suitable for large-scale production. Acetic acid, ensuring also a reasonable mechanical strength of the extrudates, seems to be more acceptable from the ecological point of view. Such surfactants as glycerol, ethylene glycol, carboxymethyl hydro cellulose were used to facilitate extrusion and to suppress generation of cracks at the drying stage. Mechanical strength was found to depend on the amount of surfactant added. As the surfactant content increases, the mean pore radius abruptly increases (Fig. 4) while integral pore volume remains constant. In the frames of the Sczukin–Rebinder concept [14,15], this trend evidences some decline in the number of interparticle contacts that decreases mechanical strength.

To check thermal shock resistance of the monoliths elaborated, the following procedure was adopted: thermally equilibrated at room temperature monolith was placed into a muffle furnace preheated to 700°C, kept here for 10 min, then rapidly (in the order of seconds) withdrawn into the air and put onto the cold ceramic plate. For all monoliths compositions, after 5–10 thermocycles of this type cracks appeared propagating mainly from the ends of monoliths along its length. To suppress cracks generation, some alumosilicate fibers were introduced into the monoliths making thus a sort of fiber reinforced ceramic. This approach efficiently improved thermal shock tolerance (more than 25 thermocycles were successively carried out without any cracks appearance).

The optimized catalysts based upon MA $LnMnO_3$ contain up to 20 wt.-% of alumina and

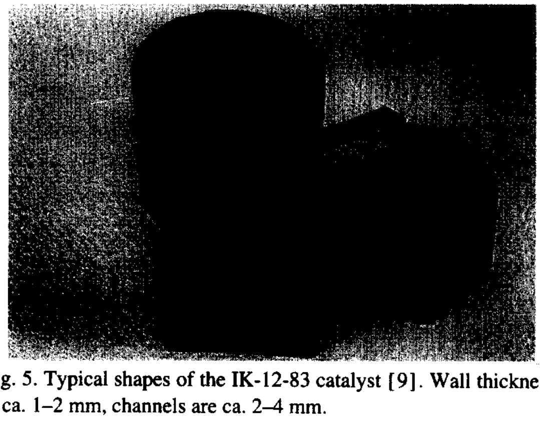

Fig. 5. Typical shapes of the IK-12-83 catalyst [9]. Wall thickness is ca. 1–2 mm, channels are ca. 2–4 mm.

up to 10 wt.-% of alumosilicate fibers. After calcination at 900°C they have specific surface values ca. 30–50 m^2/g, total pore volume up to 0.3 ml/g, mechanical strength up to 10–20 MPa (for rings) and a bulk density of ca. 1 g/ml. In the Pilot Chemical Department of the Boreskov Institute of Catalysis one of this catalysts is produced under the IK-12-83 trade mark. Typical shapes of these catalysts are shown in Fig. 5.

3.3. Catalysts testing

High thermally stable monolith perovskite catalysts were mainly developed for gas and liquid fuels combustion in turbines, power plants, boilers, etc. both in flameless and catalyst-supported regimes. Catalytic combustion allows to decrease operating temperatures up to ca. 1000°C, thus, effectively suppressing NO_x emission to a several ppm level [17]. Besides, when catalysts are used, polyaromatic compounds such as benzpyrene, etc. are totally eliminated from the gases. Moreover, combustion processes control and energy recovery can be greatly improved due to more even temperature distribution across the combustion chambers. Lean air-fuel mixtures and ballasted fuels can also be safely combusted using catalysts.

At present, the catalysts elaborated were tested mainly using bench-scale installations with quartz tube reactors equipped with one monolith up to 20 cm length. In the process of butane and gasoline combustion both in flameless and catalyst-supported regimes, IK-12-83 catalyst has operated at 900°C for 1 month without loss of activity, monolith integrity and mechanical strength [7]. Honeycomb catalysts based upon bulk lanthanum manganites (IK-12-83) were found to be the only systems without platinum group metals capable to support the process of methane flameless combustion. High efficiency of this process and low values of CO and NO_x emissions makes it promising for wide-scale application. Thus, for methane/air = 1:10 fuel mixture and GHSV ca. 12 000 h^{-1} stable operating temperature was kept at 1300°C level with flue gases CO content <300 ppm and $NO_x < 3$ppm. In these small-scale installations, for leaner methane-air mixtures stable autothermal regime of flameless combustion could be kept at temperatures as low as 900–1000°C not increasing the CO and NO_x emissions.

The other broad field of application is high-temperature incineration of toxic wastes (chemical industry, medical source and municipal wastes) and other harmful compounds including chemical weapons. For municipal waste incineration plants, these catalysts can be used to prevent dioxins formation. In the flameless regimes of combustion, incineration of such nitrogen-containing compounds as aniline and aliphatic amines was found to proceed without any noticeable NO_x emission. To check whether monolith perovskites can be used to destroy chlorinated hydrocarbons, catalytic incineration of chloroform $CHCl_3$ was studied. A stream of methane-air mixture was saturated at room temperature with $CHCl_3$ vapors and feeded into the adiabatic reactor equipped with monolithic perovskite IK-12-83. At operating temperatures around 1000°C, regime of methane flameless combustion and catalysts performance were found not to be affected by $CHCl_3$ admixture, whereas complete destruction of the latter into HCl, CO_2 and H_2O was secured.

Bulk perovskite catalysts have also revealed high tolerance to the poisoning action of HCl-containing gases even at moderate temperatures [9]. Thus pilot testing in the furnace for photomaterials combustion (in this case operating temperatures were in the range of 500–700°C) have demonstrated that after two months work bulk perovskite retained ca. 40% of the initial activity, while γ-alumina supported perovskite of the same chemical composition was nearly completely deactivated.

To understand the reasons of a rather high stability of bulk monolith perovskites in HCl-containing gases, X-ray microprobe analysis has been carried out. For both fresh and spent catalysts (Fig. 6), a spatial distribution of La and Mn is strongly correlated while that of Al varies in the opposite direction thus evidencing an absence of the chemical interaction between binder and the active component. For spent catalyst both Ag and

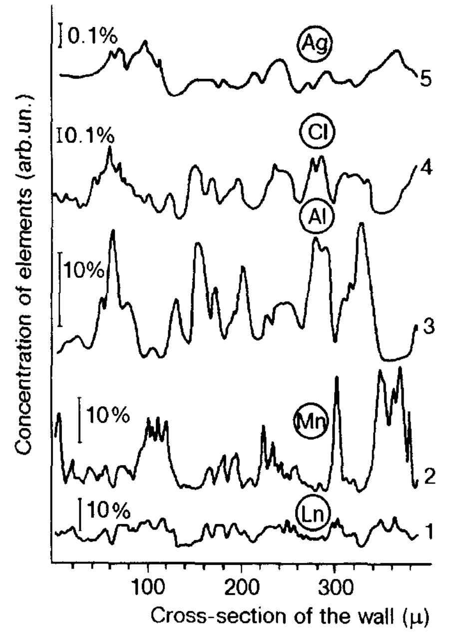

Fig. 6. X-Ray microprobe analysis of the elements distribution across the monolith perovskite wall section (spent sample).

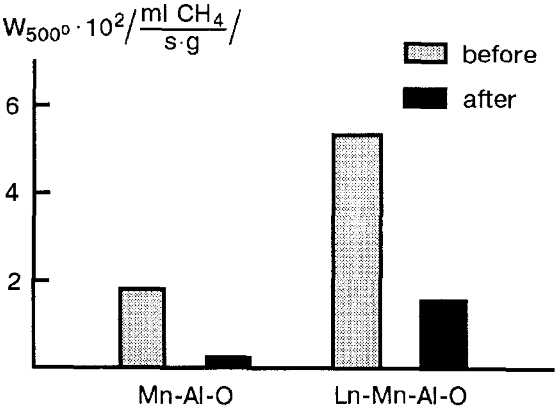

Fig. 7. Stability of the catalysts to SO_2 poisoning in the CH_4 oxidation process (0.2% CH_4, 0.05% SO_2, 10 h of testing).

Cl appear, Cl concentration being strongly correlated with that of Al. These results are in favor of the chlorine preferable location on the binder particles that explains rather high Cl-tolerance of this system. It means that in general bulk perovskites especially those with a minimum binder content are expected to be more active and stable in halogen-containing gases than any supported oxide catalysts. Rather effective accumulation of silver on the monolith walls thus preventing its loss is surely an additional advantage of using catalysts in such furnaces.

Monolith perovskites have also demonstrated high stability to the poisoning action of sulfur dioxide at moderate temperatures. Thus, Fig. 7 shows that bulk perovskite catalysts retain higher level of catalytic activity in CH_4 oxidation in the presence of SO_2 as compared with MnO_2/alumina supported catalysts.

Monolith perovskite catalysts of somewhat different compositions were found to have high activity and good stability in a number of industrial catalytic processes such as methane reforming, ammonia oxidation into nitrogen oxides, sulfur dioxide reduction, etc. (Fig. 8 and Fig. 9)

Pilot testing of honeycomb perovskites in the reaction of high-temperature (700–900°C) ammonia oxidation (initial concentration of NH_3 in the air = 10%) into nitrogen oxides (perovskites were positioned after Pt-Rh gauzes) have dem-

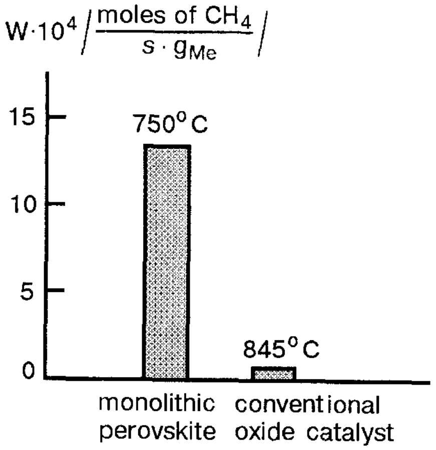

Fig. 8. Activity of the catalysts in methane CO_2 reforming after 12 h of testing (CH_4/CO_2 = 1:2).

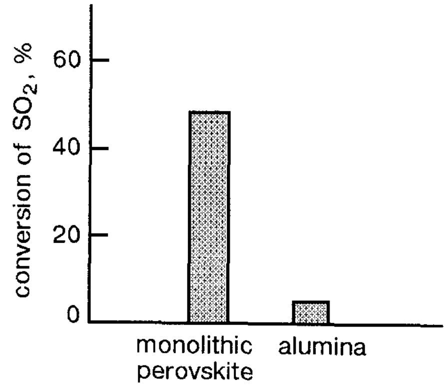

Fig. 9. Activity of the catalysts in SO_2 reduction by methane at 800°C after 10 h of testing (3% O_2, 12% CH_4, 9% SO_2, 25 000/h).

onstrated that they substantially enhance a degree of ammonia oxidation (from 86.6% to 96%) thus preventing ammonia slip and dangerous accumulation of explosive salts in the cold parts of the equipment. As a result, process safety may be considerably improved.

4. Conclusions

Highly active and stable in hostile environments monolith perovskite catalysts are elaborated. Pilot tests and bench-scale experiments have demonstrated these catalysts can efficiently operate in the temperature range up to 900–1300°C and space velocities in the range of 10 000/h in the processes of flameless fuels combustion, environmental control as well as in the industrial chemical processes.

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