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Characterization and catalytic investigation of NO + CO reaction on perovskites of the general formula $La_xM_{1-x}FeO_3$ (M = Sr and/or Ce) prepared via a reverse micelles microemulsion route

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Abstract

Four different perovskite type solids with nominal composition $LaFeO_3$ (LFOr), $La_{0.85}Sr_{0.15}FeO_3$ (LSFOr), $La_{0.8}Sr_{0.1}Ce_{0.1}FeO_3$ (LSCFOr) and $La_{0.8}Ce_{0.2}FeO_3$ (LCFOr) were prepared via a reverse micelles microemulsion route. The aim of this work was to investigate the effect of doping with Sr and Ce in the structural properties, surface area and catalytic properties of final solids in comparison with the undoped reference solid $LaFeO_3$. The microemulsion system which was used is composed of cetyl-trimethyl-ammonium-bromide (CTAB), 1-butanol, *n*-octane and nitrate salts of the metals. XRD measurements combined with Rietveld analysis helped us to identify the % quantity of structural phases which were formed. Scanning electron microscopy (SEM) images showed that the obtained solids consist of nanoparticles in the range of 20–80 nm. BET experiments showed that the final solids achieve much higher specific surface area (ssa) (30–61 m^2/g) than similar solids which have been prepared by other methods. Catalytic tests in NO + CO reaction were made with the use of gases He/NO/CO in the ratio 96/2/2 with a total flow rate of 100 cm^3/min. The full sequence of catalytic activity of tested solids is LCFOr > LSCFOr > LSFOr ≥ LFOr and this sequence is in full agreement with the sequence of increment of ssa of the solids.

Keywords: Perovskites; Ce; Sr; NO + CO; Reverse microemulsion

1. Introduction

In the mid 1970s, introduction of catalysis for the exhaust-gas treatment of an automobile opened a new area for catalytic applications. The development of catalysts for controlling both mobile and stationary sources of emissions has been accelerated due to the development of three-way catalysts (TWC) for converting HC, CO and NO_x simultaneously [1]. The need for NO_x reduction, which is one of the main topics for the catalytic control of air pollution, led to the development of new catalyst compositions containing noble metals (Pt, Rh and Pd) and cerium oxide as oxygen storage agent. Perovskite-type oxides of the general type ABO_3 are an important class of compounds and have been widely studied as far as their physical and chemical properties are concerned. Their catalytic properties have been extensively studied for oxidation and reduction reactions. The catalytic reduction of NO by CO is an important chemical process because of the need to control both NO and CO emissions from motor vehicles. This reaction has been studied extensively for perovskites. These studies have shown that to control NO and CO emissions perovskites must be placed on inert substrates. The properties of ABO_3 perovskites can be easily modified by substitution of the A site cation, usually La^{3+}, by another cation of different oxidation state such as Sr^{2+} or Ce^{4+} [2–6]. The high catalytic activity of such substituted structures is considered to be related with their defective structure and the effect of the valence alternation on the catalytic activity [7,8].

Perovskites are normally formed by physically mixing metal oxide precursors, or by coprecipitation of mixed salts, followed by calcination at high temperatures (H.T.s), typically exceeding 1000 °C. The specific surface area (ssa) of perovskite materials prepared using these techniques are low, typically lower than 5 m^2/g, which is disadvantageous for catalytic applications [2].

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By using microemulsions instead, a mixture of oil, surfactant and water as reaction medium, it is possible to synthesize nanometre-sized metal oxide precursors [9,10]. The surfactant molecules aggregate spontaneously, with water located in the core of the aggregates forming nanometer-sized water droplets that act as reactors for formation of perovskite precursor particles. Due to the dynamics of the system, the water in oil droplets are very rapidly mixed leading to formation of the particles by precipitation inside the microemulsion droplets. The perovskite can then be formed at low calcination temperature, due to the homogeneous mixing of the metals and the very small size of the primary particles. A low calcination temperature will reduce the particle growth and preserve a high surface area. The microemulsion method has been widely used in the last decade for the preparation of many kinds of solids which can be used as catalysts. A full report on this field can be found in a review article of Eriksson et al. [11] which includes all types of catalysts prepared with microemulsion method and their applications in heterogeneous catalysis.

In this work we prepared four different perovskite type oxides of the general formula $La_xM_{1-x}FeO_3$ trying to substitute the A site cation (La^{3+}) by Sr^{2+} and/or Ce^{3+} using reverse micelles microemulsion method. The nominal compositions of the final structures were $La_{0.85}Sr_{0.15}FeO_3$ (LSFOr), $La_{0.8}Ce_{0.2}FeO_3$ (LCFOr) and $La_{0.8}Sr_{0.1}Ce_{0.1}FeO_3$ (LSCFOr). In case of Sr the incorporation into the perovskite structure (LSFOr sample) was successful, but in case of Ce the incorporation was unsuccessful as it has also been observed in previous reports [12–18]. The objectives of this work were to investigate the characteristics of perovskite materials when prepared using the microemulsion technique and to test the catalytic performance of the materials in the catalytic reaction of the reduction of NO by CO. The characterization and catalytic results of the above three perovskite oxides were compared with the corresponding results of a $LaFeO_3$ (LFOr) perovskite oxide which has also been prepared via microemuslion technique and has previously been reported [19]. The results were also compared with the results of similar solids which have been prepared via the microemulsion method by other workers [20] and with similar solids prepared by other methods.

2. Experimental

2.1. Microemulsion used and preparation of samples

The microemulsion A (see Table 1) used for the preparation of the solids was based on the cetyl-trimethyl-ammonium-bromide (CTAB)/1-butanol/*n*-octane/$Fe(NO_3)_3 + B(NO_3)_x$ system, where B = La and/or Sr, Ce. In this microemulsion A a second microemulsion B based on CTAB/1-butanol/*n*-octane/NH_3 was added under stirring at room temperature. After several conductivity tests [21] we reached the conclusion that the compositions of microemulsion shown in Table 1 were worthwhile for the synthesis of the corresponding perovskites and their subsequent comparison. The selected compositions for every solid are listed in Table 1.

The precipitation took place by adding the microemulsion B to A, where B contains NH_3 in excess for the precipitation of the corresponding hydroxides.

The prepared precursor phases were then filtered, dried at room temperature, heated at 800 °C for 4 h under atmospheric conditions, and ground in an agate mortar in order to obtain the final solids. The final calcination temperature (800 °C) was selected after thermogravimetric experiments. Above this temperature no mass loss was observed.

2.2. XRD analysis—Rietveld analysis

In order to check the development of the crystal phases the XRD patterns of the prepared materials were obtained after heating at 800 °C for 4 h. The equipment used was a Brüker Advance D8 system employing Cu Kα radiation ($\lambda = 1.5418$ Å). The samples were placed in quartz sample holders and the step scans were taken over the range of 2θ angles from 10 to 90° in steps of 0.02° (2θ). The XRD patterns were assigned using the Joint Committee on Powder Diffraction Standards (JCPDS) database and then were analyzed with Rietveld refinement using an applicable computer program.

2.3. Surface area

The specific surface area S_p (m^2/g) was estimated by N_2 adsorption–desorption porosimetry at 77 K via the BET method. The instrument employed was a Fisons 1900 Sorptomatic system. Prior to the measurement, the sample (~250 mg) was degassed overnight at 200 °C under pressure *P* of 10^{-2} bar.

2.4. Scanning electron microscopy (SEM) images

The obtained solids after calcination at 800 °C were observed by scanning electron microscopy using a JEOL JSM 5600 instrument.

Table 1
The quantities of the components (CTAB, 1-butanol, *n*-octane and aqueous phase) of microemulsions A and B, respectively, used for the preparation of perovskites

Microemulsion components	Microemulsion A	Microemulsion B
Surfactant: CTAB (g)	38.4	36
Oil phase: *n*-octane (ml)	114	142.5
Cosurfactant: 1-butanol (ml)	32	30
Aqueous phase A: $Fe(NO_3)$ 0.8 M–$La(NO_3)_3$/$B(NO_3)_x$[a] 0.8 M (ml)	16	–
Aqueous phase B: NH_4OH 8 N (ml-M) (ml)	–	20

[a] B = Sr and/or Ce, *x* = oxidation state of metal B.