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# Methane conversion and $SO_2$ resistance of $LaMn_{1-x}Fe_xO_3$ ($x = 0.4$, 0.5, 0.6, 1) perovskite catalysts promoted with palladium

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## Abstract

Lanthanum perovskites were synthesized by malic acid complexation and different amounts of palladium were added by dry-wet impregnation. Measurements of methane conversion on fresh and $SO_2$-treated perovskite catalysts were made between 25 and 500 °C. Methane conversion on fresh catalysts commenced at ~300 °C, and the best activities were achieved with low loadings of palladium. The B-site metal combinations $Mn_{0.4}Fe_{0.6}$ and $Mn_{0.6}Fe_{0.4}$ showed better conversion activity than $Mn_{0.5}Fe_{0.5}$ and Fe. All fresh perovskite catalysts except those with 10% Pd gave 100% conversion of methane at 500 °C. The resistance of 10% Pd perovskite catalysts to sulfur was generally better than that of catalysts with low Pd loadings. This was due to the high Pd coverage on the perovskite surface. Fresh and $SO_2$-treated $LaMn_{0.4}Fe_{0.6}O_3$ perovskite catalysts promoted with 2 and 2.5% of palladium exhibited the highest activities for methane conversion.

*Keywords:* Perovskite; Methane conversion; $SO_2$ poisoning

## 1. Introduction

Catalytic combustion requires the use of active catalysts to remove less active compounds such as methane and so maintain the autothermal reaction [1]. At low temperatures, methane and other unburned hydrocarbons are removed via catalytic oxidation [2–5]. Under these conditions $Pd/Al_2O_3$ is reportedly one of the most active noble metal catalysts for methane oxidation in the presence of oxygen excess [2].

Perovskite catalysts are considered to be a promising alternative catalyst for methane combustion because of their low cost, thermal stability at relatively high temperatures, and catalytic activity [3,6]. The structural formula of perovskite is $ABO_3$ with various cations in A- and B-sites. The A-site cations are usually rare earth or earth metals and the B-site cations are first row transition metals. Ability to alter the catalytic properties of perovskites by partial substitution of the A- and B-sites metals [7–11] makes them of considerable interest for exhaust [8,12–15] and natural gas [1,16–23] cleaning processes. Since sulfur species are always present in these processes resistance to sulfur poisoning is an important property for an effective catalyst.

Although, sulfur poisoning of perovskite catalysts is a recognized problem in exhaust gas cleaning, the low concentration of sulfur in natural gases enables the use of perovskite catalysts in methane combustion [18]. The conversion of methane and the resistance of the catalyst to sulfur have been studied with various combinations of A- and B-site metals and by promoting perovskites with MgO. In most studies the A-site metal has been lanthanum, substituted with a small amount of Sr or Ce, and the B-site metal has been manganese or cobalt. In studies on the promoting effect of MgO, the B-site metal has been Mn, Mg, and/or Cr. Several studies [1,16–23] have indicated that appropriate combination of A- and B-site metals or the use of MgO has a promotive effect on the methane conversion activities and resistance to sulfur poisoning.

Palladium addition on the B-site reportedly [2] has little influence on methane conversion activity at <500 °C. It has been suggested that the $LaTi_{0.5}Mg_{0.5-x}Pd_xO_3$ perovskite structure favors the activity of small Pd particles via changes in the lattice

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oxygen contribution and possible local changes in the Pd oxidation state. The effects of sulfur on the $LaTi_{0.5}Mg_{0.5-x}Pd_xO_3$ ($0 \leq x \leq 0.1$) perovskites were not studied.

The methane conversion and $SO_2$ resistance of lanthanum-based perovskite catalysts at low temperatures were studied in this work, while changes were made in combination of the B-site metals and the amount of impregnated noble metal. The study was focused on the balance between the composition of perovskite and the amount of impregnated noble metal on the surface of the catalyst. The possibility to improve the resistance of the perovskites to sulfur through Pd loading on the surface was investigated. The information will be useful in the design of new cost-efficient catalysts for methane combustion.

## 2. Experimental

### 2.1. Synthesis of perovskites

Sol–gel method and malic acid were used to synthesize $LaMn_{0.6}Fe_{0.4}O_3$, $LaMn_{0.5}Fe_{0.5}O_3$, $LaMn_{0.4}Fe_{0.6}O_3$, and $LaFeO_3$ perovskites. The method has been described previously [10,11]. Stoichiometric amounts of commercially available nitrates were dissolved in water. After all solids were dissolved, malic acid was added to the solution in an amount 1.5 times the total amount of the metal ions. After the malic acid was dissolved, the pH of the solution was adjusted to 2.35–2.75 with $NH_3$. The pH was dependent on the precipitation point of the mixture. The excess water was evaporated with a rotavapor at 70 °C. The intermediate product was dried 4 h in sandbath at 150 °C and calcined in air for 5 h at 750 °C. After the calcination was complete, palladium was impregnated to the synthesized perovskite by dry-wet method.

### 2.2. Characterization

Structures of the prepared lanthanum perovskites were determined with an X-ray powder diffractometer (Bruker-AXD D8 Advance). Scanning rate was $0.6^\circ\ min^{-1}$ and Cu Kα radiation was used. The Brunauer–Emmett–Teller (BET) surface areas of the synthesized perovskites were measured with a Micromeritics ASAP 2010 device. The measuring was carried out by nitrogen adsorption. Before BET measurement, samples (~150 mg) were evacuated at 350 °C overnight. Scanning electron microscopy (FE-SEM, Hitachi S4800) was used to characterize the surface of the perovskites.

#### 2.2.1. Methane conversion measurement

Methane conversion measurements were carried out in a custom-made continuous flow quartz reactor system. The system is illustrated in Fig. 1. There are small claws in the quartz tube, fiberglass was placed against them and then the reactor was packed with catalyst. In measurements of $CH_4$ conversion the total flow rate of 1.04% $CH_4$/16.00% $O_2$/82.96% $N_2$ mixture gas was $1200\ ml\ min^{-1}$. The flow was adjusted with a Bronkhorst Hi-Tec mass flow controller. The quartz reactor and catalyst sample (~600 mg) were heated in a Meyer pipe oven at 500 °C ($\Delta T = 14.3\ °C\ min^{-1}$). The gas samples were taken at 22–25 (room temperature), 100, 200, 300, 400, and 500 °C and analyzed by gas chromatography (GC, HP 6890 plus) with multicolumn. The flow of methane mixture gas was directed to sample tubes with a seven-way valve.

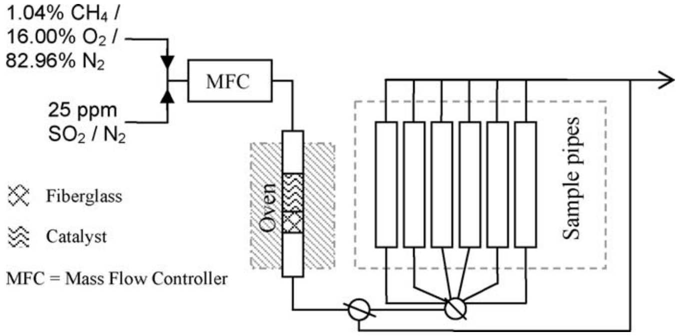

Fig. 1. Reactor system for methane conversion measurements.

Studies on $SO_2$ treatment of the perovskite catalysts were made in the same reactor system as measurements of $CH_4$ conversion. Contamination of the sample tubes with $SO_2$ was avoided by bypassing them during sulfur treatment. The flow of 25 ppm $SO_2/N_2$ mixture gas was controlled with a mass flow controller and the flow rate was $1200\ ml\ min^{-1}$. The catalyst sample was held at 450 °C for 30 min. After the sample was cooled down to room temperature the $SO_2$ mixture gas was changed to methane mixture gas and the methane conversion measurement was carried out.

## 3. Results

Powder X-ray studies of the synthesized lanthanum perovskites showed that in all cases the cubic structure of perovskite was formed during calcination. The pH of the reactant solution, measured surface areas, and length of the edge of the lattice cell (*a*) of the synthesized perovskites are reported in Table 1. After calcination, palladium was added to the surface of synthesized La-perovskite by dry-wet method. The amounts of impregnated palladium were 2, 2.5, 5, and 10%.

### 3.1. Effect of palladium on $CH_4$ conversion

Catalytic activity of perovskite can be increased through the addition of a small amount of noble metal to the structure [7,8,10]. Methane conversions on fresh lanthanum perovskite catalysts promoted with 2, 2.5, 5, or 10% of palladium (Fig. 2a) indicated that the best conversion activities were achieved with

Table 1
Data obtained from the prepared perovskites

| Perovskite | pH of reactant solution | Surface area ($m^2\ g^{-1}$) | *a* (Å) |
|---|---|---|---|
| $LaMn_{0.6}Fe_{0.4}O_3$ | 2.62 | 17.6 | 3.85 |
| $LaMn_{0.5}Fe_{0.5}O_3$ | 2.63 | 10.1 | 3.89 |
| $LaMn_{0.4}Fe_{0.6}O_3$ | 2.64 | 17.1 | 3.90 |
| $LaFeO_3$ | 2.50 | 12.3 | 3.93 |

*Note*: *a*, length of the edge of the lattice cell.