

Methane conversion and SO₂ resistance of LaMn_{1-x}Fe_xO₃ ($x = 0.4, 0.5, 0.6, 1$) 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 SO₂-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 SO₂-treated LaMn_{0.4}Fe_{0.6}O₃ perovskite catalysts promoted with 2 and 2.5% of palladium exhibited the highest activities for methane conversion.

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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/Al₂O₃ 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 ABO₃ 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_xO₃ 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 $\text{LaTi}_{0.5}\text{Mg}_{0.5-x}\text{Pd}_x\text{O}_3$ ($0 \leq x \leq 0.1$) 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 $\text{LaMn}_{0.6}\text{Fe}_{0.4}\text{O}_3$, $\text{LaMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$, $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$, 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 $0.6^\circ \text{min}^{-1}$ and $\text{Cu K}\alpha$ 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 ($\Delta T = 14.3^\circ\text{C min}^{-1}$). The gas samples were taken

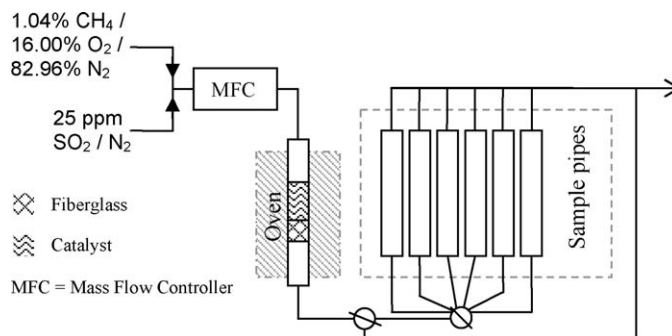


Fig. 1. Reactor system for methane conversion measurements.

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.

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 ($\text{m}^2 \text{g}^{-1}$)	a (\AA)
$\text{LaMn}_{0.6}\text{Fe}_{0.4}\text{O}_3$	2.62	17.6	3.85
$\text{LaMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$	2.63	10.1	3.89
$\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$	2.64	17.1	3.90
LaFeO_3	2.50	12.3	3.93

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

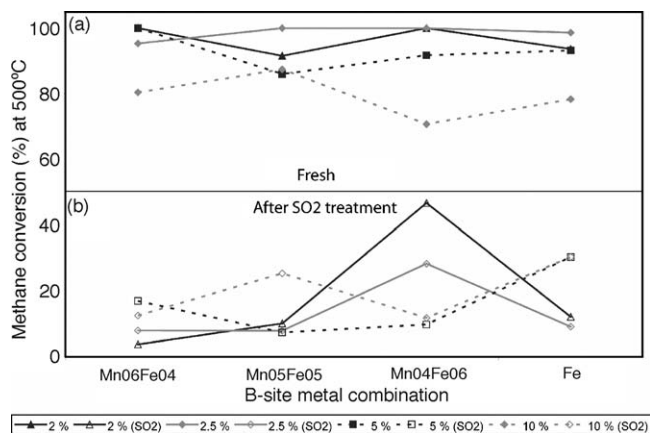


Fig. 2. Effect of Pd concentration on methane conversion activity of Pd-promoted perovskite catalysts at 500 °C.

low loading of noble metal. Differences in the methane conversions of low-loaded catalysts (2–5% Pd) were slight and, with one exception, the highest conversion activities were obtained with perovskite catalysts promoted with 2.5% Pd. The exception was in the series of $\text{LaMn}_{0.6}\text{Fe}_{0.4}\text{O}_3$ perovskites, where the best activity was obtained with 5% Pd loading. The differences in conversion activities of the low-loaded (2–5% Pd) $\text{LaMn}_{0.6}\text{Fe}_{0.4}\text{O}_3$ perovskites were small, however.

Methane conversions of the prepared perovskites commenced at ~ 300 °C except for 2.5% Pd/ $\text{LaMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$, 2% Pd/ $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$, and 2.5% Pd/ $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$ where the beginning of CH_4 conversion occurred at 200–250 °C. The methane conversion figures for $\text{LaMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ perovskite promoted with various amounts of palladium are presented in Fig. 3. No hysteresis behaviour was observed as a function of reversed temperature ramp (from 500 to 25 °C).

Fig. 4 shows that the methane conversion activity as a function of B-site metals combination varies with the amount of Pd. Highest conversion activity can be obtained with the B-site metal combinations $\text{Mn}_{0.4}\text{Fe}_{0.6}$, $\text{Mn}_{0.5}\text{Fe}_{0.5}$, and $\text{Mn}_{0.6}\text{Fe}_{0.4}$. Comparison of the surface area of perovskites (Table 1) with the observed activities (Fig. 4) clearly shows that there is no correlation between them.

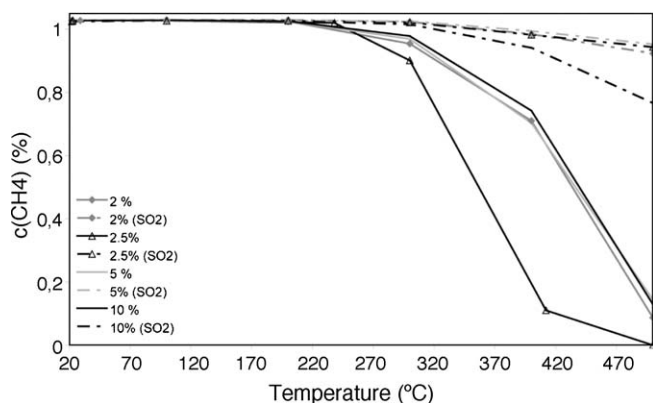


Fig. 3. Methane conversion figures at 20–500 °C for fresh and SO_2 -treated $\text{LaMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ perovskite catalysts promoted with 2, 2.5, 5, and 10% Pd.

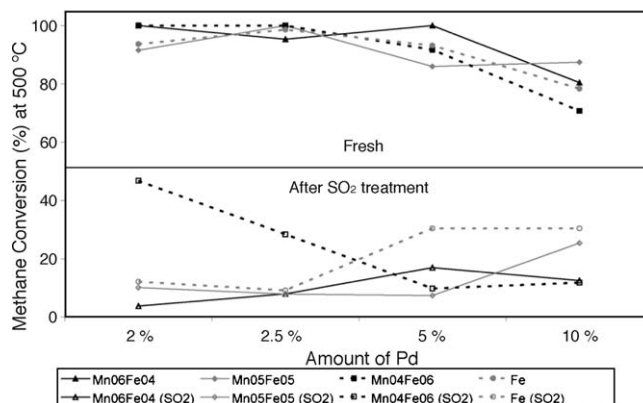


Fig. 4. Effect of B-site metals on methane conversion with Pd-promoted La-perovskites.

SEM investigations revealed that increase in the amount of Pd on the surface of the perovskites causes changes in dispersion and particle size of Pd. The SEM images of 2, 5, and 10% Pd/ $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$ are shown in Fig. 5. As can be seen the Pd particles (small light spots) are evenly spread over the surface. The spots are agglomerated Pd particles. When the amount of palladium was increased, the sizes of Pd agglomerates increased from ~ 5 nm (2% Pd) to ~ 15 nm (10% Pd). Pd-promoted active surface sites were correlated with decreasing CH_4 conversion activity, suggesting that altered interaction between Pd and the surface active sites of perovskite may influence the oxidation and reduction properties of the catalyst.

The average heights of the agglomerates can be estimated from the surface areas and agglomerate coverage on the surface. The heights 0.8 nm for 2% Pd loading, 1.3 nm for 5% Pd, and 1.9 nm for 10% Pd in the case of $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$ perovskite are in qualitative agreement with the SEM observations.

3.2. Effect of SO_2 treatment on CH_4 conversion

The measurements of CH_4 conversion on SO_2 -treated Pd-supported lanthanum perovskite catalysts revealed deactivation. The methane conversion activities of prepared $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($x=0.4, 0.5, 0.6, 1$) perovskites as a function of palladium loading are summarized in Fig. 2b. The drop in methane conversion activities of the SO_2 treated perovskites relative to the fresh ones was notable, at 500 °C between 53 and 96%. The highest CH_4 conversion activity after SO_2 treatment was measured for 2% Pd/ $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$ catalyst (47% at 500 °C).

Unlike the case of fresh palladium perovskite catalysts, after the SO_2 treatment there were no clear trends between the loading of Pd and the methane conversion. Among the fresh lanthanum catalysts, conversion activities were lowest for those with 10% Pd but in general, SO_2 treatment did not depress the activities of these catalysts as much as the activities of the catalysts with lower Pd concentration. Two catalysts did not fit this generalization: 2 and 2.5% Pd/ $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$. Fig. 4 reveals that LaFeO_3 catalysts with 5 and 10% Pd have higher methane conversion than 2.5% Pd/ $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$.

Several studies [1,3,20,22] have suggested that in the first step of sulfur poisoning the SO_2 reacts with the perovskite oxide sur-

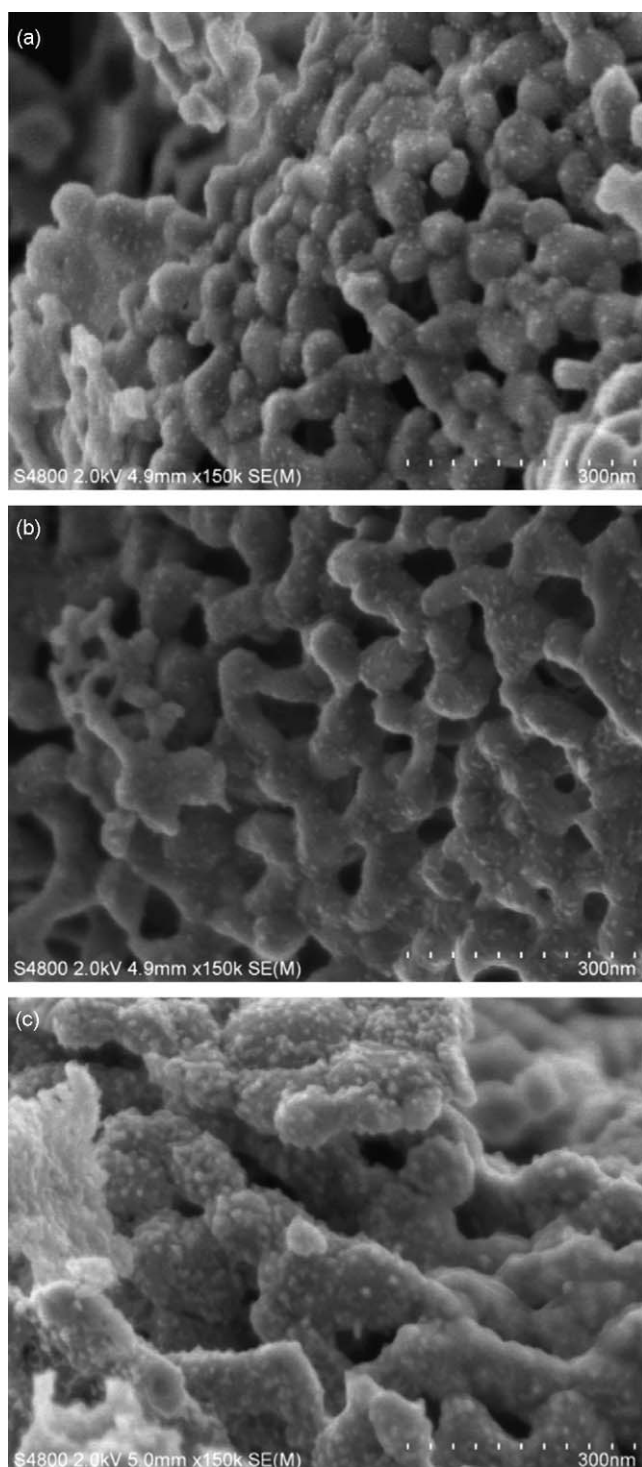


Fig. 5. SEM images of $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$ promoted with different amounts of Pd: (a) 2% Pd, (b) 5% Pd, and (c) 10% Pd.

face. Reactive species (SO_2^- , SO^-) formed during adsorption are considered to react with surface oxygen of the perovskite to form SO_3^- radicals. It has also been reported that some of the formed species are thermally unstable and react with oxygen (SO_4^-) or desorb at high temperatures. Studies on SO_2 poisoning of $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$ perovskites [22] revealed the formation of lanthanum sulfate and cobalt oxide during poisoning, and

increase in the concentration of sulfates with reaction temperature. The irreversible formation of sulfates is accompanied by pore blockage [3].

In our study the time during, which perovskite catalysts were exposed to SO_2 , was too short detection of lanthanum sulfates. Elemental analysis of randomly chosen samples showed that the sulfur content of the poisoned catalysts were $<0.5\%$. Our suggestion is that the higher content of palladium on the surface of the perovskites protects the adsorption sites. First, the sulfur reacts with the palladium particles through shell progressive mechanism, and after all palladium is covered the formation of lanthanum sulfates commences. Corresponding reaction behaviour has been reported for SO_2 poisoning of $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskite [23]. The protecting effect of palladium for the active sites could explain why the methane conversion activity decreased less with 10% than the 2 and 2.5% palladium catalysts when these were treated with SO_2 .

4. Conclusions

The best catalyst candidates for methane conversion were 2 and 2.5% Pd-promoted lanthanum perovskites with B-site metal combination $\text{Mn}_{0.4}\text{Fe}_{0.6}$. The fresh catalysts achieved 100% conversion activity at 400°C . The methane conversion activities of $\text{LaMn}_{0.4}\text{Fe}_{0.6}\text{O}_3$ promoted with 2 and 2.5% Pd were still higher than activities of other studied perovskites after SO_2 treatment. The SEM images showed that the coverage and the particle size of Pd on the surface of perovskite increased as a function of noble metal loading. A relationship between activity and amount of promoting Pd can be deduced from the SEM images. The methane conversion of the prepared lanthanum catalysts decreased as the loading of promoting Pd increased. The interaction between surface and promoter decreased with the loading of Pd owing to the greater height of the Pd agglomerates. The findings indicate the possibility of preparing perovskite catalysts suitable for methane combustion in industrial scale by optimizing the composition of the A- and B-site metals with low loading of Pd promoter.

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