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Effect of A-site metal on methane combustion on 2% Pd / $AMn_{1-x}Fe_xO_3$ (A = Ba, La, Pr; x = 0.4, 0.6, 1) perovskites

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Barium, lanthanum, and praseodymium perovskites were prepared by malic acid complexation. Surface areas of the La and Pr perovskites were between 17.1 and 21.6 $m^2 g^{-1}$. The moderate low surface areas (5.7 $m^2 g^{-1}$) observed for corresponding barium perovskites were due to the high calcination temperatures. The calcination temperature also affected the shapes and sizes of the perovskite particles. According to SEM images the nanoparticles of the La and Pr perovskites were spherical, whereas those of barium perovskites were flakes. The conversion of methane increased in the order of A-site metal Ba < Pr < La. The CH_4 conversion after SO_2 treatment correlated with size of the perovskite particles: the smaller the particles the better the activity. The highest methane conversion after SO_2 treatment was achieved with lanthanum perovskite with B-site metal combination $Mn_{0.4}Fe_{0.6}$.

KEY WORDS: perovskite; methane combustion; SO_2 poisoning.

1. Introduction

Methane, CH_4, is removed form exhaust gas stream by using catalytic oxidation. Pd/Al_2O_3 is reported to be the most active catalyst for methane oxidation when excess of oxygen is present. The use of perovskites in methane combustion has been investigated, as well [1–14]. The effect on methane combustion of the A-site metal in perovskites has been studied by substituting lanthanum with another metal [1,2,9,15,16]. The CH_4 conversion of fresh lanthanum perovskites is reported to compare with that of commercial Pd/Al_2O_3 catalysts. Substitution of another metal for lanthanum increases both methane combustion and the resistance of sulfur.

Sulfur poisoning of perovskite oxides can be expected during combustion of methane from exhaust gas. The resistance of perovskites to sulfur is dependent on the composition of the A- and B-site metals [2,3,17,18], and different metal combinations have been studied in the hope of improving the resistance of perovskite to sulfur.

In previous work, we investigated the effects on methane conversion of adding palladium on lanthanum perovskite and adjusting the B-site metal combinations [19]. Highest activity was achieved with low loading of Pd (2% or 2.5%) and with the B-site combination $Mn_{0.4}Fe_{0.6}$. The differences activities of low Pd loaded perovskite catalysts were minor. The CH_4 conversion of the studied lanthanum perovskites dropped sharply after SO_2 treatment. The perovskite catalysts $LaMn_{0.4}Fe_{0.6}O_3$ promoted with 2% or 2.5% Pd and $LaFeO_3$ promoted with 5% or 10% Pd maintained their conversion activity better than other perovskites that were studied.

Our aim in this work was to determine the effect of metal combination of perovskite on sulphur resistance by changing the A-site metal. Low temperature CH_4 conversion activity and SO_2 resistance were studied for barium, lanthanum, and praseodymium perovskites promoted with 2% Pd. Information about the factors improving methane conversion, and especially about factors improving sulfur resistance, is required in the development of new catalysts for natural gas or exhaust gas cleaning applications. Although, several investigations have suggested that the resistance of perovskites to sulfur can be improved by partial substitution of lanthanum, little attention has been paid to the possibility of improving sulfur resistance of perovskites by chancing the A-site metal.

2. Experimental

2.1. Sample preparation

Perovskites were prepared via malic acid complexation, as in our previous studies [19,20]. Stoichiometric amounts of reactants, which were commercially

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available nitrates, were dissolved in water. Malic acid was then added to the solution. After the malic acid was dissolved, NH_3 was added to adjust the pH of the solution. The pH was dependent on the precipitation point of the solution. In this study the pH of solutions was between 2.5 and 3.0. In the case of lanthanum and praseodymium perovskites, excess of water was evaporated with rotavapor at 70 °C. The intermediate product that formed was dried in a sandbath at 150 °C for 4 h and calcined in air at 750 °C for 5 h. Barium perovskite were prepared by the same method except that the pH of the solution was adjusted to 9. After adjustment of pH the solution was mixed for 24 h before removal of excess water. The Ba perovskites required higher calcination temperature than the La and Pr perovskites. Calcination was done at 950 °C. 2% of palladium was added to the synthesized perovskites using dry-wet impregnation.

2.2. Characterization

Structures of the perovskites were determined with a powder X-ray diffractometer (Bruker-AXD D8 Advance) using CuK_α radiation; the scanning rate was $0.6° \text{ min}^{-1}$. Surface studies of perovskites were carried out with a Micromeritics ASAP 2010 (Brunauer–Emmett–Teller, BET, surface areas) and a Hitachi S4800 scanning electron microscopy (FE-SEM). The perovskite samples ($\sim$ 150 mg) were evacuated at 350 °C overnight before determination of BET surface areas.

2.3. Methane conversion measurements

A custom-made continuous flow quartz reactor system was used in the methane conversion and sulfur poisoning measurements. The reactor system was illustrated in our previous study [19]. In methane conversion studies, 1.04% CH_4/16.00% O_2 / 82.96% N_2 mixture gas (from Air Liquide) was used and SO_2 treatment was made with 25 ppm SO_2/N_2 mixture (AGA). The total flow rate in both treatments was 1200 ml min^{-1} and the flow was controlled with a Bronkhorst Hi-Tec mass flow controller.

In methane conversion measurements, perovskite samples (600 mg) were heated at 500 °C ($\Delta T = 14.3 \text{ °C min}^{-1}$) in a Mayer pipe oven. The gas samples were collected at room temperature (22–25 °C) and at 100, 200, 300, 400, and 500 °C. Samples were analyzed with a HP 6890 Plus gas chromatograph (GC).

SO_2 treatments were done with the same reactor system. After measurements of methane conversion, the system was cooled down to room temperature under methane mixture gas stream. Then the streaming gas was changed to SO_2 mixture gas. Perovskite samples were heated to 450 °C in 35 min and held at that temperature for 30 min. Finally, the system was cooled down and the methane conversion measurements were carried out for poisoned perovskite samples.

3. Results

3.1. Characterization of catalysts

The synthesis parameters and the measured properties of the perovskites are summarized in table 1. Comparison of surface areas of the perovkites shows that surface areas were notably smaller for the barium perovskites than the corresponding lanthanum and praseodymium perovskites. The smaller surface areas were due to the agglomeration of particles caused by the 200 °C higher calcination temperature for the barium perovskites [20]. Surface areas were higher for of perovskites with manganese in B-site. According to the measured data (table 1), there was a correlation between the amount of iron and the length of the edge of the lattice cell (*a*): the higher the iron content, the longer the edge. After calcination of the perovskites, palladium was added to the surface by dry-wet impregnation.

SEM images of surfaces of the perovskites show how the A-site metal affects the shape of the particles. SEM images of 2% Pd/$AMn_{0.4}Fe_{0.6}O_3$ (A = Ba, La, Pr) are presented in figure 1. As can be seen, the particles of La and Pr perovkites are spherical, as in our previous study [19], while those of barium perovskites particles are flake-like. The different shape and size of the barium perovskite particles might be due to the modification of the preparation method: higher pH and longer mixture time of solution and higher calcination temperature (causing agglomeration) were needed to obtain the cubic structure of barium perovskites. The shape of the nanoparticles may also be influence by the A-site metal because particles of Pr perovskites were not as spherical as those of lanthanum even though syntheses were carried out under the same conditions. As seen in figure 1b, some flakes of Pr perovskites are present, as well. The impregnated palladium is evenly spread over the surface, and Pd particles appear as small white granules on the surfaces of the prepared catalysts. The particle size of the perovkites increased in the order La < Pr < Ba.

Table 1
Data obtained from barium, lanthanum, and praseodymium perovskite

Perovskite	pH of reactant solution	Calcination temperature (°C)	Surface area ($m^2\ g^{-1}$)	a (Å)	Amount of Pd (%)
$BaMn_{0.6}Fe_{0.4}O_3$	9.0	950	5.7	3.86	2
$BaMn_{0.4}Fe_{0.6}O_3$	9.0	950	5.7	3.92	2
$BaFeO_3$	9.0	950	2.8	4.03	2
$LaMn_{0.6}Fe_{0.4}O_3$	2.6	750	17.6	3.85	2
$LaMn_{0.4}Fe_{0.6}O_3$	2.6	750	17.1	3.90	2
$LaFeO_3$	2.5	750	12.3	3.93	2
$PrMn_{0.6}Fe_{0.4}O_3$	3.0	750	17.6	3.87	2
$PrMn_{0.4}Fe_{0.6}O_3$	2.8	750	21.6	3.88	2
$PrFeO_3$	2.5	750	14.1	3.89	2

a length of the edge of the lattice cell.

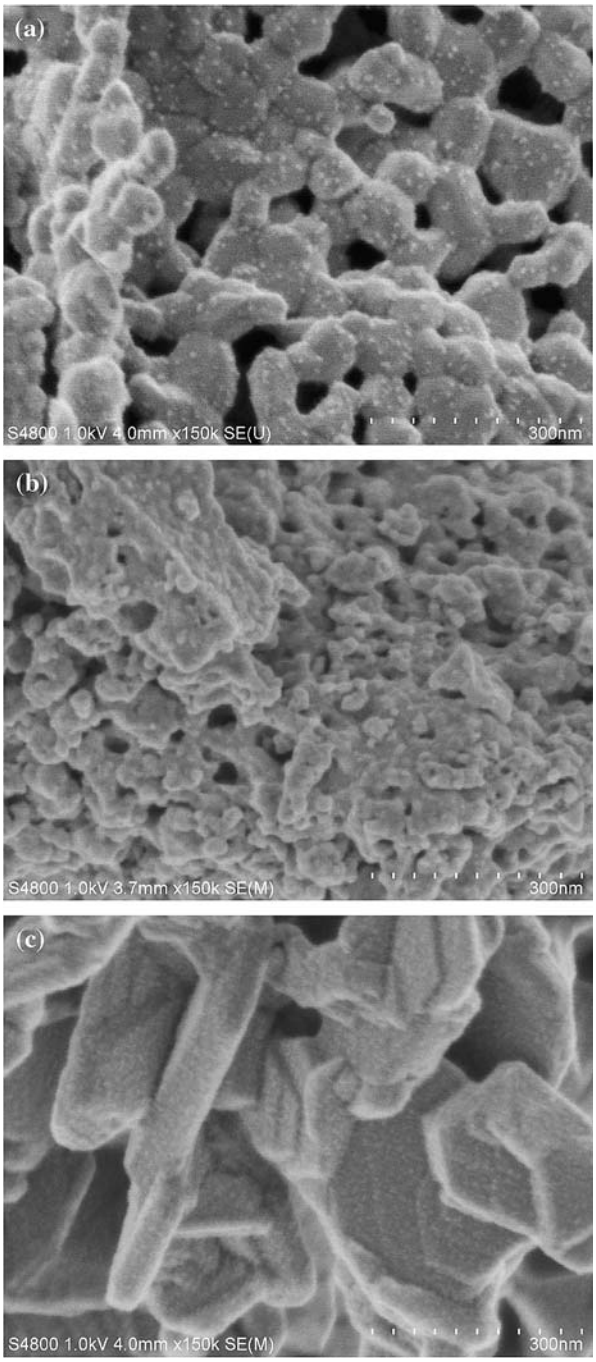

Figure 1. SEM images of 2% Pd / $AMn_{0.4}Fe_{0.6}O_3$ (A = Ba, La, Pr) perovskites (magnification 150 k): (a) La, (b) Pr, and (c) Ba.

3.2. CH_4 conversion measurements

In our previous study [19] we studied the effect of palladium as promoter in lanthanum perovskite. The results showed that greater amount of palladium leads to growth of Pd agglomerates on the surface, which cover the active sites of perovskite and weaker the interaction between noble metal and the perovskite surface. The weaker interaction decreased the activity of the fresh catalyst. Generally, the resistance to sulfur was better for lanthanum perovskites with 10% loading of Pd than for perovskites with lower noble metal content. However, the highest activity after SO_2 treatment was achieved with 2% and 2.5% Pd / $LaMn_{0.4}Fe_{0.6}O_3$ catalysts at 500 °C in our previous study [19]. It has been suggested that the deactivation of palladium catalyst by sulfur compounds is due to Pd–S interactions [21,22]. This being the case, increased amount of palladium on the surface would protect the perovskite from sulfur poisoning.

In the present work the effect of A-site metal on CH_4 conversion activity was studied with barium, lanthanum, and praseodymium perovskites promoted with 2% Pd. In the cases of La and Pr perovskites, the fresh state conversion commenced at 250–300 °C, whereas after SO_2 treatment methane conversion did not begin before ~ 350 °C. Sulfur treatment decreased activity. The drop in conversion was less abrupt with lanthanum than praseodymium perovskites. It has been suggested that sulfur dioxide reacts with surface oxides [2,3,18,19]. Reaction between SO_2^- or SO^- species (which can be form during adsorption) and surface oxygen of perovskite generates SO_3^- radicals, and at high temperatures SO_3^- radicals may desorb or react further with oxygen to yield SO_4^{2-}. The interaction between surface sulfate species and perovskite can lead to A-site metal sulfate. The activity of perovskite can be returned by decomposition of sulfur compound at high temperature (> 900 °C) [3].

Figure 2 shows the methane conversion of fresh and SO_2-treated perovskites at 500 °C. The figure reveals that 100% conversion can be achieved with fresh lanthanum and praseodymium perovskites with combination of manganese and iron ions in the B-site.

The methane conversions of fresh and SO_2-treated barium perovskites were below 10% and conversion started at > 400 °C. The lower activity of barium perovskites than of La and Pr perovskites may be due to smaller surface areas or the shape and size of Ba particles. The SEM images showed the surface structures of barium perovskites to be less porous than those of lanthanum perovskites, which had highest fresh and SO_2-treated

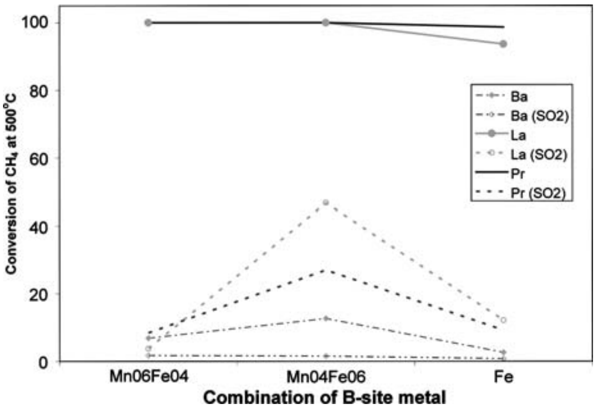

Figure 2. Methane conversion of Ba, La, and Pr perovskites promoted with 2% Pd as a function of B-site metal combination.

methane conversion of the perovskites. The methane conversion and resistance to sulfur increased (Ba < Pr < La) as the particle size of the perovskites decreased.

In our previous study [19], increased coverage of Pd agglomerates on the surface of lanthanum perovskite decreased conversion activity of the fresh catalyst, but it also improved sulfur resistance. The suggestion was that higher palladium content (10%) on the surface of the perovskite altered the interaction between promoter and support, thus changing the oxidation and reduction properties of noble metal particles on active surface sites. The deactivation was observed as decreased activity in methane conversions. When the catalyst is treated with SO_2, the sulfur reacts with palladium through shell progressive mechanism. The palladium layer covered the surface of the perovskite as evidenced in the less pronounced drop in CH_4 conversion with 10% Pd than with low Pd loading (2–5%).

Our studies indicate that the highest methane conversion activity can be achieved with perovskites with 2% loading of Pd, where the A-site metal is lanthanum and the B-site metal combination is $Mn_{0.4}Fe_{0.6}$. The resistance to sulfur might be increased by partial substitution of lanthanum.

4. Conclusions

The lanthanum perovskite with B-site metal combination $Mn_{0.4}Fe_{0.6}$ exhibited highest methane conversion activity in this study. Conversions of the fresh perovskites were better for lanthanum and praseodymium perovskites than for barium perovskites. The differences in activity were due to surface areas and shape and size of perovskite particles. SEM images revealed that the barium perovskite particles were flake-like and larger than the spherical particles of La and Pr. A-site metal increased the resistance to sulfur in the order (Ba < Pr < La). Correlation of sulfur resistance with particle size revealed better CH_4 conversion after SO_2 treatment for perovskite with smaller particle size. Modification of the A-site metal is a useful way to improve the sulfur resistance of perovskite catalyst.

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