

## Partial Oxidation of Methane Over the Perovskite Oxides

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**Abstract:**  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Ti}_{0.2}\text{O}_{3-x}$  oxides were synthesized by a combined EDTA-citrate complexing method. The catalytic behavior of these two oxides with the perovskite structure was studied during the reaction of methane oxidation. The pre-treatment with methane has different effect on the catalytic activities of both the oxides. The methane pre-treatment has not resulted in the change of the catalytic activity of BSCFO owing to its excellent reversibility of the perovskite structure resulting from the excellent synergistic interaction between Co and Fe in the oxide. However, the substitution with Ti on Fe-site in the lattice makes the methane pre-treatment have an obvious influence on the activity of the formed BSCTO oxide.

**Keywords:** Methane oxidation,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ ,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Ti}_{0.2}\text{O}_{3-x}$ , perovskite.

### Introduction

The conversion of methane to syngas is a very appealing route for the conversion of the large reserves of natural gas<sup>1</sup>, from which a wide variety of valuable hydrocarbons and oxygenates, such as methanol and formaldehyde, can be synthesized. A great research effort is presently being carried out on the catalytic partial oxidation of methane to syngas<sup>2</sup>. In the present work, two oxides with the perovskite structure,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Ti}_{0.2}\text{O}_{3-x}$  were systematically investigated for the partial oxidation of methane in order to explain the difference in catalytic activity resulting from the interaction between cobalt and metal substitute B-site (Fe or Ti).

### Experimental

The catalyst powders  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Ti}_{0.2}\text{O}_{3-x}$  (abbreviate as BSCFO and BSCTO, respectively) were synthesized using a combined citric acid and EDTA complexing method, which was previously reported in detail<sup>3</sup>.

The crystal structures of the fresh or used samples were characterized with an X-ray diffractometer (XRD, Rigaku D-Max/RB), using Cu K $\alpha$  radiation.

Oxidation and reduction properties of catalysts were studied by the oxygen temperature-programmed desorption technique (O<sub>2</sub>-TPD) and the temperature programmed reduction (TPR).

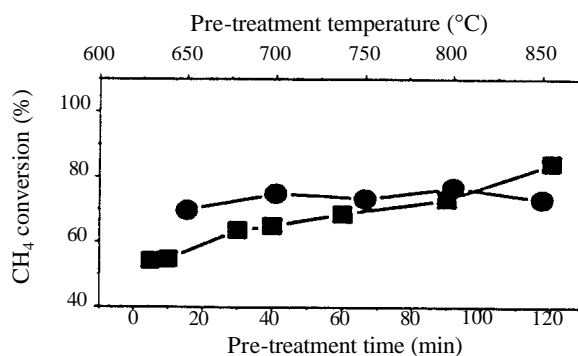
The purpose of the re-oxidation treatment is to reveal the oxidation properties of the reduced sample. Before re-oxidation, the sample was reduced in a flow of 5% H<sub>2</sub>-Ar mixed gas at a heating rate of 10°C/min up to 1050°C. Subsequently, the temperature of the sample was decreased to 850°C in the protection of Ar and the gas flow was simultaneously switched to 1% O<sub>2</sub>-Ar mixture for a desired period of time (*i.e.* 12 h, 6 h, 3 h, 1.5 h and 0.5 h). The temperature of the sample was decreased to 100°C. Finally, TPR of re-oxidation sample was carried out. The amount of H<sub>2</sub> uptake in TPR was estimated from the integrated peak areas by comparison with those obtained by using pure LaCoO<sub>3</sub>.

The catalytic reactions were carried out at atmospheric pressure in a continuous flow quartz reactor. The exit gases were analyzed by an on-line gas chromatograph (HP 4890D) equipped with a thermal conductivity detector and carbon sieve columns.

### Results and Discussion

It is interesting to note that methane pre-treatment time has a significant effect on the activity of the BSCTO catalyst. With increasing methane pre-treatment time, the activity of the catalyst was increased significantly (**Figure 1**). The conversion of CH<sub>4</sub> varied from about 50% to 80% as the pre-treatment time increased from 5 min to 120 min. This result suggests that during the CH<sub>4</sub> treatment, BSCTO catalyst can be decomposed slowly and reduced into metal Co (after experiment, pink metal Co was found on the wall of the reaction tube), which is responsible for the formation of the catalytic products. We have also found that the temperature did not affect the activity of catalyst significantly (**Figure 1**). This further suggests that BSCTO catalyst is very unstable and the metal Co in BSCTO is very easy to be reduced. If the pre-treatment time is long enough, for example, 120 min for this reaction, the active metal can be completely reduced even if the pre-treatment temperature is as low as 650°C.

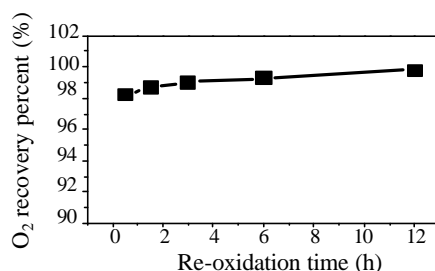
**Figure 1** The effect of the pre-treatment time (■) and temperature (●) on the activities of BSCTO catalyst (reaction temperature 850°C)



In addition, as mentioned above, methane pre-treatment has hardly effect on catalytic properties of BSCFO catalyst, which may be attributed to the quick recovery of its perovskite structure under the reaction condition that is an atmosphere of coexistence

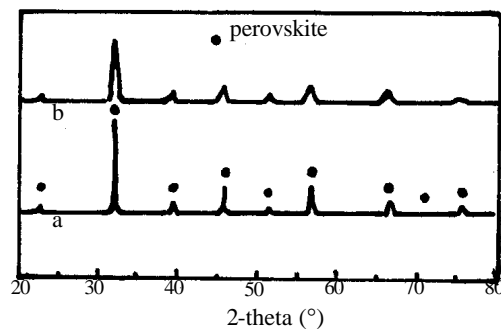
of reductive ( $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CO}$ ) and oxidative compound ( $\text{O}_2$  and  $\text{CO}_2$ ). Z. P. Shao *et al.*<sup>3</sup> have pointed out that catalyst exists an excellent reversibility of the phase structure under reaction condition for BSCFO. We investigated the effect of re-oxidation treatment on TPR profiles of reduced catalysts in order to explain the recovery of the oxygen content in the sample. For BSCFO, the re-oxidation treatments at different time do not effect the hydrogen consumption peak position and area of the catalyst. The perovskite structure of the sample can be recovered after every re-oxidation. Through the quantitative calculation, we found that the oxygen content can almost reach to oxygen content in the fresh sample (see **Figure 2**) after every re-oxidation. Even after 0.5 h re-oxidation in 1%  $\text{O}_2$ -Ar mixture, the oxygen recovery percent of sample can reach to 98%.

**Figure 2** Oxygen recovery percent of BSCFO catalyst after re-oxidation for different time in 1%  $\text{O}_2$ -Ar mixture



In order to further rationalize the structure reversibility of the BSCFO, their XRD features have been carried out. The XRD profiles of the fresh sample and the sample suffering  $\text{H}_2$ -TPR and re-oxidation five times are shown in **Figure 3**. The XRD showed BSCFO sample can be quickly convert to its original structure after re-oxidation due to the excellent synergistic interaction between Co and Fe in the catalyst. Under our reaction conditions, the atmosphere in the reactor is both reductive and oxidative, because of the coexistence of reductive ( $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2$ ) and oxidative ( $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) compounds, the reduced catalyst is re-oxidized and a redox process occurs over the working catalyst.

**Figure 3** X-ray diffraction patterns of BSCFO catalyst.

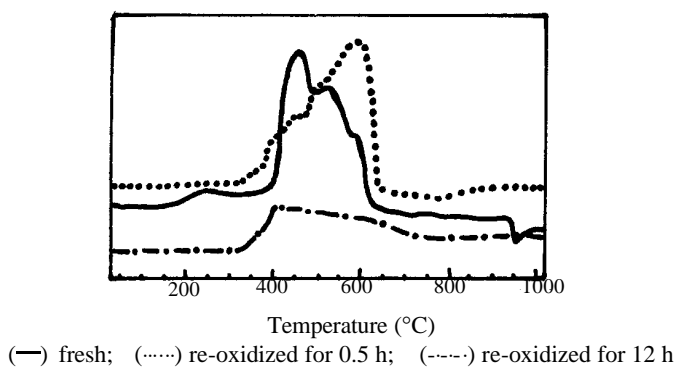


(a) fresh sample; (b) recycled re-oxidized sample for 5 times

The experiment showed that the methane pre-treatment has no effect on its catalytic activity due to the quick reversibility of the perovskite structure of BSCFO catalyst in the atmosphere of our experiment.

However, for BSCTO sample, the case is very different. **Figure 4** shows the effect of re-oxidation time on TPR profiles of reduced catalyst. The H<sub>2</sub>-TPR profile of reduced BSCTO sample after re-oxidation reveals a more pronounced alternation compared with the fresh sample, even the re-oxidized time increased, the TPR profile does not reach the aspect of the fresh sample, which features five peaks. On the basis of experiment results, we suppose that it is much more difficult for reduced BSCTO sample to restore to its original perovskite structure. The XRD results further confirmed this propose. As mentioned above, we can suggest that the structure reversibility of the sample decides whether the pre-treatment of reductive gas, CH<sub>4</sub>, plays or does not play a role on their activities.

**Figure 4** H<sub>2</sub>-TPR profiles of BSCTO catalyst



## References

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