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ORIGINAL PAPER

Effect of the preparation method on the catalytic performance of $Ca_3Co_4O_9$ for methane oxidation

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Abstract The layered structure oxide $Ca_3Co_4O_9$ particle was synthesized by two routes of citrate sol–gel method. The structure, morphology and surface property of $Ca_3Co_4O_9$ was characterized by XRD, SEM and XPS, respectively. The catalytic activity of $Ca_3Co_4O_9$ for methane combustion was tested in a fixed bed quartz tubular microreactor. The catalysis results reveal that the catalytic activity is sensitive to the texture of $Ca_3Co_4O_9$ by different route. TG measures confirm that the small particle size of $Ca_3Co_4O_9$ favors the oxygen transformation on the surface, which can be ascribed the random distribution of the crystal axes in irregular $Ca_3Co_4O_9$ particle.

Keywords $Ca_3Co_4O_9$ · Citrate sol–gel method · Methane · Catalytic combustion

1 Introduction

Recently, the misfit layered cobalt oxides $Ca_3Co_4O_9$ has received considerable attention due to its excellent thermoelectric property [1, 2]. Many efforts have been devoted to fabrication of textured $Ca_3Co_4O_9$ ceramics or single crystals of $Ca_3Co_4O_9$ and their thermoelectric properties [3–6]. On the other hand, it is reported that the $Ca_3Co_4O_9$ shows large range oxygen content variation depending on the temperature and partial pressure of oxygen [3, 7]. However, the property of oxygen nonstoichiometry in the misfit-layered calcium cobalt oxides has not paid more attention to.

Catalytic oxidation of methane over metal oxides catalysts is an environmental friendly reaction because of a relatively low CO_2 emission for the same amount of energy production and lower NO_x formation in energy production. Some investigations indicate that the lattice oxygen is likely to be involved in the catalytic oxidation over cobalt oxide [8], and the reaction follows the Mars–Van Krevelen redox mechanism [9]. In this work, we prepared polycrystalline $Ca_3Co_4O_9$ material by two routes of citrate gel method and evaluated catalytic property of as-prepared $Ca_3Co_4O_9$ for methane oxidation reaction, with the aim to investigate the catalytic activity of oxygen vacancy and effect of particle texture on the catalytic property.

2 Experimental

2.1 Preparation

The $Ca_3Co_4O_9$ was synthesized by two routes of citrate gel method.

$Ca_3Co_4O_9$-A: An aqueous solution containing calcium and cobalt nitrate (Ca/Co molar ratio = 0.75), and citric acid (citric acid/(Ca + Co) = 1.3) was gradually heated to 80 °C resulting in the formation of a gel. The gel was kept at this temperature for 4 h with stirring and dried at 120 °C for 12 h. The dried was burned using anhydrous ethanol as the igniter. The obtained ash was pulverized and then calcined at 900 °C for 10 h.

$Ca_3Co_4O_9$-B: In this method, a dispersant of polyethylene glycol (PEG) 400 (2% volume ratio) was added in the mixture solution of metal ions and citric acid (similar to Process A). The solution was heated at 80 °C to obtain the

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gel. The gel was dried at 120 °C for 12 h and then heat treated in the air at 500 °C for 2 h. Finally, the ash was calcined at 900 °C for 9 h.

2.2 Characterization

The crystalline structure of the catalysts was characterized by X-ray diffraction (XRD) using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5406$Å) (Rigaku D/Max-γA, Japan). The morphology of the particles was examined using field emission scanning electron microscopy (JEOL 6500F). X-ray photoelectron spectroscopy (XPS) measurements were performed with Mg $K\alpha$ (1,253.6 eV) as the exciting radiation (ESCALAB Mark II, VG). Thermogravimetric analyses (TGA) were performed for the as-air-synthesized sample in a nitrogen stream at a heating rate of 10 °C min^{-1} (STA449C, Netzsch).

2.3 Catalysis test

Catalytic tests were carried out in a fixed bed reactor constituted of a quartz tube with an inner diameter of 4 mm at the atmospheric pressure. The feed consisted of a mixture of 2 mol% CH_4, 20 mol% O_2 and N_2 balance, with total gas hourly space velocity (GHSV) of 76,000 h^{-1}. The effluent composition was determined using on-line gas chromatography (Shimadzu, GC-14C) using a thermal conductivity detector (TCD) equipped with two columns, in which N_2, O_2 and CH_4 were separated by 5 A molecular sieve column and CO_2, C_2H_4 and C_2H_6 by GDX-502 column.

3 Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of two as-prepared $Ca_3Co_4O_9$ samples. The XRD patterns show same polycrystalline misfit layered cobalt oxides $Ca_3Co_4O_9$ structure (JCPDS File Card No. 23-0110) mainly. There was no evident diffraction peak referring to $Ca_3Co_2O_6$, or CaO and CoO. However, a small amount of $Ca_2Co_2O_5$ phase (JCPDS File Card No. 37-0668) was found in two of samples. The $Ca_2Co_2O_5$ is reported to exhibit a considerably same misfit layered crystal structure with $Ca_3Co_4O_9$ possessing 25% Ca site vacancy [10]. Thus, the most diffraction peaks of the two phases are overlapped. The c-lattice parameter, computed using d-spacing values of (00l) reflections, was found to be 10.83 Å, which is in agreement with the reported value [1].

Figure 2 shows the SEM micrographs of the $Ca_3Co_4O_9$-A and $Ca_3Co_4O_9$-B particles. It is obvious that the dispersant and heat treatment condition has distinct effects on the crystal growth though are plate-like particles observed at higher magnification micrograph ((b) and (d)). $Ca_3Co_4O_9$-A sample is irregular in size distribution and shape of particles. In comparison, the $Ca_3Co_4O_9$-B sample is homogeneous and high textured.

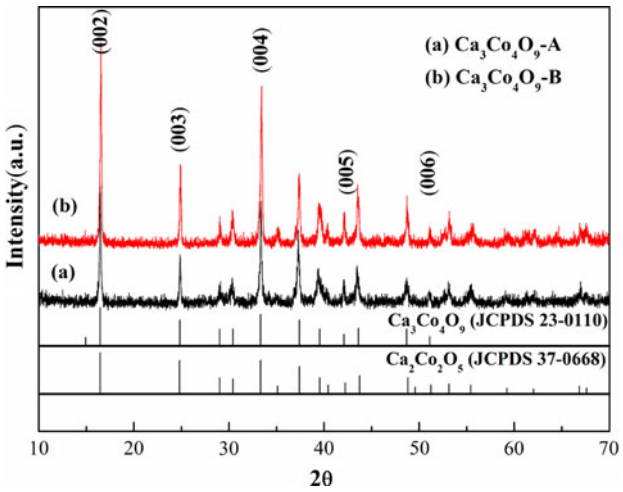

Fig. 1 XRD patterns of $Ca_3Co_4O_9$

Figure 3 presents CH_4 conversion plots obtained over two $Ca_3Co_4O_9$ samples. It can be seen that two samples exhibited a remarkable difference in methane oxidation reaction at the same condition. $Ca_3Co_4O_9$-A is more active than $Ca_3Co_4O_9$-B, the light-off temperature was about 500 °C, T_{10} and T_{90} were 575, 725 °C respectively. In contrast, the light-off temperature was about 700 °C in $Ca_3Co_4O_9$-B.

It is well accepted that gas-phase oxygen molecules are activated through an interaction with the surface of the catalyst for methane deep oxidation over metal oxides [11]. At first, the surface oxygen species on $Ca_3Co_4O_9$ was studied by XPS O1 s spectrum. As shown in Fig. 4, two samples reveal almost same surface oxygen property; a good curve fitting is obtained with three resolved O1s XPS peaks. The first peak with low binding energy ($\sim$529.1 eV) corresponded to CoO_2 layer on the surface. The second peak at binding energy ($\sim$531.3 eV) is usually ascribed to CaO layer species on the surface [12]. The minimal peak at binding energy about 533.4 eV may be assigned to adsorbed water molecules from humidity. Therefore, it can be concluded that the oxygen species on $Ca_3Co_4O_9$ surface don't cause the difference of catalytic oxidation of methane at this condition.

Secondly, we investigated the oxygen transformation on the surface of $Ca_3Co_4O_9$ by thermoanalysis measure of the as-synthesized $Ca_3Co_4O_9$ in a flowing nitrogen stream, as shown in Fig. 5. The overall weight loss observed in two samples can be divided into three processes from room temperature to 1,000 °C. The first weight loss before 500 °C could be assigned to desorption of the surface

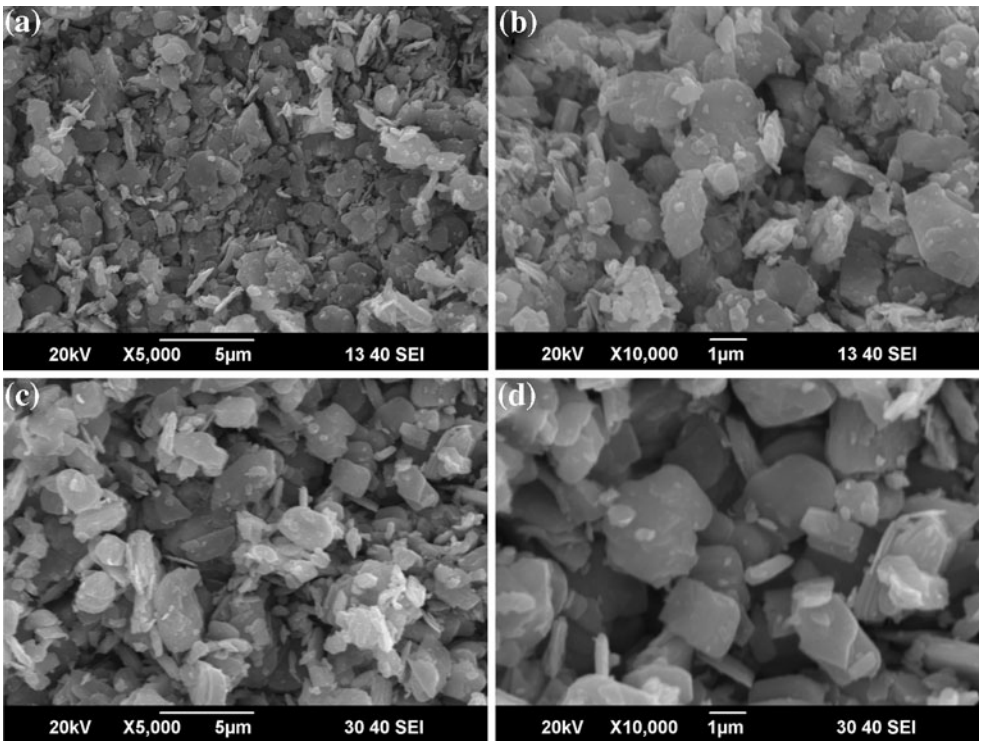

Fig. 2 SEM micrographs of $Ca_3Co_4O_9$ particles. **a**,**b** $Ca_3Co_4O_9$-A; **c**,**d** $Ca_3Co_4O_9$-B

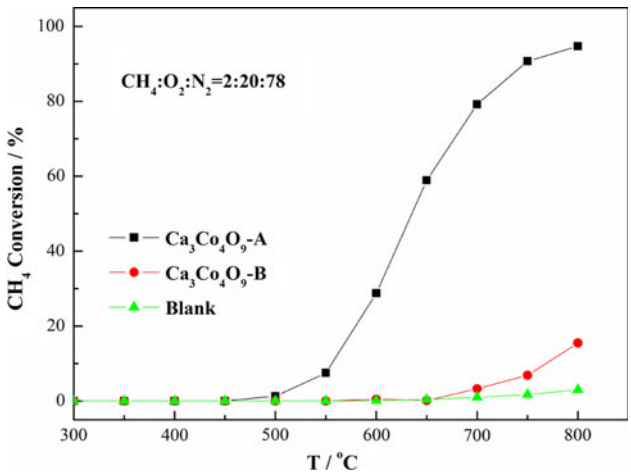

Fig. 3 CH_4 conversion plots over $Ca_3Co_4O_9$

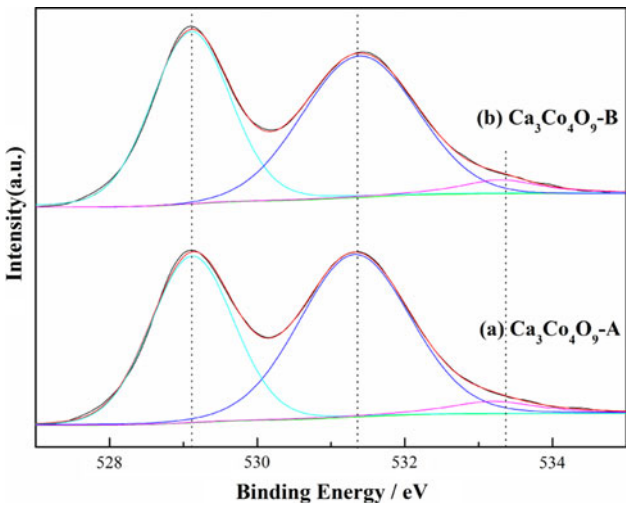

Fig. 4 XPS spectrums of $Ca_3Co_4O_9$ for the O1 s regions

adsorbed oxygen species, which is adsorbed in the structure defects (oxygen vacancies). It is notable that at about 510 °C there is a small but visible change in the slope of the TG curve. The same phenomenon has been observed by Y. Morita and is suggested as a possible phase transition point [13]. The second weight loss between 500 and 850 °C can be accounted for loss of surface lattice oxygen resulting in oxygen vacancy formation. The third weight loss possessing two successive weight losses between 850 and 1,000 °C is assigned to the decomposition of $Ca_3Co_4O_9$. Although the $Ca_3Co_4O_9$ phase transforms to $Ca_3Co_2O_6$ phase at 950 °C in air atmosphere [14], it is predictable that the decomposition temperature of $Ca_3Co_4O_9$ will move towards lower temperature in nitrogen atmosphere. Therefore, $Ca_3Co_4O_9$ was likely to decompose to $Ca_3Co_2O_6$ at 850 °C firstly, and then, $Ca_3Co_2O_6$ decomposed to CaO and CoO finally.

However, two samples gave different dynamic behavior of oxygen desorption during N_2 annealing. The weight loss in $Ca_3Co_4O_9$-A is bigger than that in $Ca_3Co_4O_9$-B at the same condition suggesting that desorption of oxygen

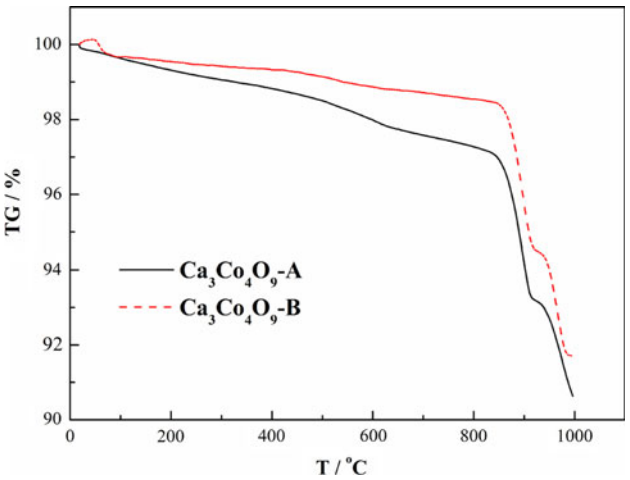

Fig. 5 TGA curves of the fresh $Ca_3Co_4O_9$ sample in flowing nitrogen

species in $Ca_3Co_4O_9$-A is easy. $Ca_3Co_4O_9$ has a layered structure in which two different kinds of Co–O layers alternate in the direction of the c-axis. In one of the layers, Co atom is in an octahedral configuration and the octahedral are edge-shared (CoO_2 layers). In the other layers, Ca, Co and O form triple rock-salt ($Ca_2CoO_{3+\delta}$) layers [5]. M. Karppinen et al. [13, 15] investigated the oxygen non-stoichiometry of the $Ca_3Co_4O_9$ and supposed that all vacancies are in the CoO layer of the insulating Ca_2CoO_3 block. In this block, the CoO layer is sandwiched in between two CaO layers. As a result, the oxygen exchange between gas and crystal lattice in small particle of $Ca_3Co_4O_9$-A is easier than that of $Ca_3Co_4O_9$-B by the random distribution of the crystal axes, as given by

$$2O_2(g) + 4V_O^{\bullet\bullet} + 8Co^{3+} \Leftrightarrow 4O_{lattice}^{2-} + 8Co^{4+}$$

4 Conclusions

Two layered structure oxide $Ca_3Co_4O_9$ particles were successfully synthesized by different routes of citrate gel method. XRD and XPS confirmed there was no obvious difference in structure and surface oxygen property for two samples. The catalytic tests revealed that two $Ca_3Co_4O_9$ particles exhibit distinct activity for combustion of methane. Based on the SEM results and TGA data, we suppose that small irregular $Ca_3Co_4O_9$ particle with random distribution of the crystal axes favors the oxygen transformation on the surface and catalytic activity.

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