Synthesis of manganese-based nanoperovskites and their application to aerobic oxidation of methane

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Abstract: The development of simple and efficient synthetic methods for preparation of high-surface-area perovskites is an important research subject in the field of heterogeneous catalysis with mixed metal oxides. Herein, hexagonal $SrMnO_3$ with high surface area is successfully synthesized by simple calcination of the amorphous precursor prepared using *aspartic acid* and metal *acetates* instead of metal *nitrates* without pH adjustment. The specific surface area reaches up to ca. 50 $m^2 g^{-1}$, which is much larger than those for $SrMnO_3$ synthesized by previously reported methods. The catalytic activity for aerobic oxidation of methane is improved in comparison with the polymerized complex method.

Keywords: Perovskite, Methane oxidation, Manganese.

1. Introduction

Perovskite-type oxides with the general formula ABO_3 are a class of mixed oxides that exhibit compositional and structural variety. The versatility and accessibility of perovskite-type oxides have attracted significant interest in broad fields of piezoelectric, ferroelectric, (anti)ferromagnetic, catalytic, and semiconducting materials. A number of methods for the synthesis of perovskites such as solid-state, coprecipitation, sol-gel, hydrothermal, freeze/spray drying, and microwave methods have been developed. In particular, an increase of surface area is important for catalytic applications and many efforts have been made to synthesize nanoperovskites with high surface area. The sol-gel methods represented by the Pechini method and the polymerized complex method are one of the most studied and frequently used techniques for the preparation of nanoperovskites because these methods can accurately control the final composition and yield pure and homogeneous perovskites.[1] Recently, we have reported the successful synthesis of hexagonal $SrMnO_3$ with high surface area by simple calcination of the amorphous precursor prepared using aspartic or malic acid and metal acetates instead of metal nitrates without pH adjustment.[2] Herein, we report the synthesis and characterization of hexagonal $SrMnO_3$ nanoperovskites and their catalytic application to aerobic oxidation of methane.

2. Experimental

Hexagonal $SrMnO_3$ nanoperovskites were synthesized by the polymerized complex, malic acid-aided, and aspartic acid-aided methods and abbreviated as SMO-PC, SMO-MA, and SMO-AA, respectively.[1,2] Each sample was characterized by elemental analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy (IR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetry-differential thermal analytical (TG-DTA), H_2 temperature-programmed reduction (H_2-TPR), and N_2 adsorption-desorption measurements. The nanoperovskite catalysts were tested for their activity in aerobic oxidation of methane in an atmospheric-pressure single-pass quartz microflow reactor. The feed mixture was delivered by thermal mass flow controllers and consisted of $CH_4/O_2/N_2$ = 1/2/8 at a total flow rate of 11 sccm. The product composition was analyzed by an online gas chromatograph equipped with a Porapak-QS, Porapak-N, and Molsieve-5 Å columns employing thermal conductivity detectors.

3. Results and discussion

The powder XRD patterns for SMO-PC, SMO-MA, and SMO-AA were in good agreement with that for the reported hexagonal $SrMnO_3$ phase [space group *P*63/*mmc*]. Impurity phases of other manganese oxides and $SrCO_3$ were not observed. The Raman spectrum of each SMO samples showed bands at 634 and 433 cm^{-1}, assignable to the A_{1g} and E_{1g} modes, respectively, which are characteristic of a Mn_2O_9 moiety. Elemental analysis using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that the molar ratio of Sr/Mn is ca. 1/1. The specific surface areas of SMO-PC, SMO-MA, and SMO-AA calculated from a Brunauer-Emmett-Teller (BET) plot of the N_2 adsorption isotherm (77 K) were up to 25, 42, and 47 $m^2\ g^{-1}$, respectively, and these values were was much larger than those of previously reported $SrMnO_3$ catalysts. The calcination temperature of precursors for SMO-AA and SMO-MA to obtain pure SMO was 823 K and lower than that (923 K) for SMO-PC. Figure 1 shows SEM images of SMO. The nanoparticles of SMO-AA and SMO-MA obtained at 823 K have spherical-like morphology and were estimated to be 10–40 nm. On the other hand, the sintering of SMO nanoparticles was observed in the case of SMO-PC obtained at 923 K. All these results suggest that the formation of amorphous precursor by using the dicarboxylic acid with lower carbon content would be important to obtain the pure SMO at low calcination temperature.

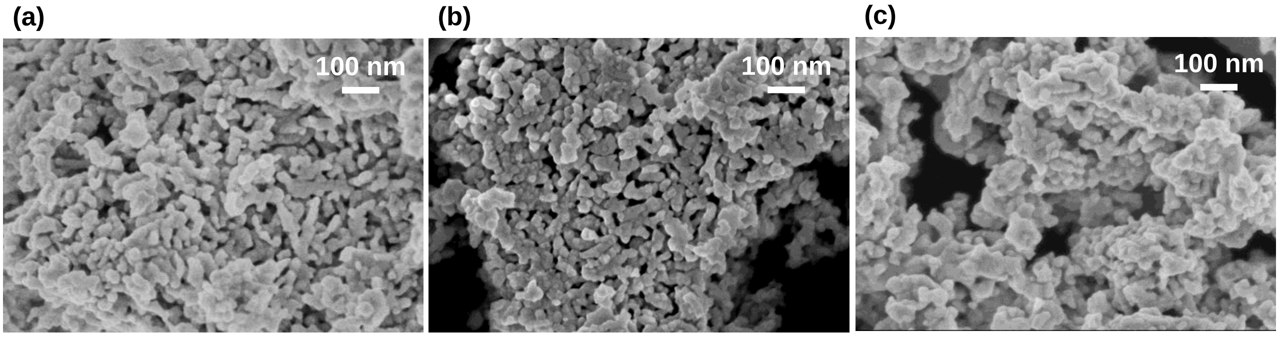

Figure 1. SEM images of (a) SMO-AA, (b) SMO-MA, and (c) SMO-PC.

The catalytic reactivity of SMO-AA, SMO-MA, and SMO-PC was compared for the aerobic oxidation of methane. Only carbon dioxide (CO_2) was formed, and the formation of other selectively-oxygenated products such as methanol, formaldehyde, formic acid, and carbon monoxide (CO) were not observed. Among the catalysts tested, SMO-AA showed the highest activity. The reactivity of SMO decreased in the order of SMO-AA > SMO-MA > SMO-PC, in good agreement with the trends of reactivity for liquid-phase aerobic oxygenation of fluorene. These results indicate that the synthetic methods and specific surface areas of SMO would play an important role in the present methane oxidation.

4. Conclusions

In conclusion, SMO with high surface area was successfully synthesized by the amino acid-aided method. The specific surface area of SMO-AA reached up to 47 $m^2\ g^{-1}$, which is the highest value among the previously reported SMO samples. The catalytic activity of SMO for aerobic oxidation of methane was improved.

References

1. S. Kawasaki, K. Kamata, M. Hara, ChemCatChem 8 (2016) 3247.
2. K. Sugahara, K. Kamata, S. Muratsugu, M. Hara, ACS Omega 2 (2017) 1608.