



Short Communication

Preparation and catalytic activities of the novel double perovskite-type oxide $\text{La}_2\text{CuNiO}_6$ for methane combustionRuisheng Hu^{a,*}, Ranran Ding^a, Jie Chen^a, Jianan Hu^a, Yulong Zhang^b^a School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, PR China^b Western Research Institute, 365 N 9th St, Laramie, WY, USA

ARTICLE INFO

Article history:

Received 17 November 2011

Received in revised form 11 January 2012

Accepted 12 January 2012

Available online 21 January 2012

Keywords:

Rare earth

Double perovskite-type oxide

Methane catalytic combustion

ABSTRACT

Rare earth perovskite-type oxides $\text{La}_2\text{CuNiO}_6$ and LaNiO_3 were prepared by a sol–gel method and investigated as catalysts for the combustion of methane. The obtained powders were characterized by XRD, H_2 -TPR, XPS and M techniques. XRD data shows that both $\text{La}_2\text{CuNiO}_6$ and LaNiO_3 formed single-phase perovskite-type oxides. The experimental results show that the catalytic activity of $\text{La}_2\text{CuNiO}_6$ was much higher than that of LaNiO_3 because of the different structure and surface properties. This study points out a potential way to develop more active double perovskite-type catalysts for the combustion of methane.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Methane is not only the main component of natural gas as a highly economical energy source, but also present at low concentrations in many fugitive emissions requiring further treatment to prevent pollution [1]. As a heat source for various chemical processes, conventional flame combustion has several problems such as emission of NO_x and unburned hydrocarbons, as well as low energy efficiency [2]. Catalytic combustion has very attractive characteristics compared with flame combustion, due to its higher energy conversion efficiency and ultra-low emissions of environmental pollutants [3]. With a catalyst, the combustion temperature is lower and the combustion is performed at a concentration range outside of flammability limits [4]. A variety of catalyst systems have been developed for catalytic combustion to pursue suitable catalysts with high thermal stability and activity [5].

At present, methane catalytic combustion materials are mainly concentrated on three kinds of catalysts including noble metal, supported metal oxide and composite metal oxide. In methane catalytic combustion, although noble metal-based catalysts show very high specific activity [6,7], their utilization in combustors is limited by their high costs, high volatility of pure metals and their oxides, and the tendency toward to sintering at moderate temperature. Compared to noble metal catalysts, perovskite-type catalytic materials have attracted considerable interests for many years due to their high activity and thermal stability in the catalytic total oxidation of hydrocarbons. Generally, perovskite-type catalysts were divided

into single perovskite compounds (ABO_3) and double perovskite compounds ($\text{A}_2\text{B}'\text{B}''\text{O}_6$). The double perovskite-type oxides have more variations than the single perovskite-type oxides. The greater variation may promote catalytic chemistry for double perovskite-type catalysts. Kobayashi [8] reported that double perovskite-type oxide $\text{Sr}_2\text{FeMoO}_6$ had colossal magnetoresistance at room temperature, which had attracted great attention. The physics community carried out a large number of extensive researches about the electrical, magnetic and transport properties of such materials [9,10]. In contrast, the chemical sector did little research about double perovskite-type oxides. In 2004, Falcón et al. [11] first reported that $\text{Sr}_2\text{FeMoO}_6$ could be used as a catalyst in methane combustion synthesized with a citric acid decomposition method. At 527 °C the methane conversion rate was as high as 80%. However, little work had been published on the double perovskite-type oxides as the catalysts of methane combustion since then. In this work, the rare earth double perovskite-type oxide $\text{La}_2\text{CuNiO}_6$ was prepared to examine its catalytic behavior for the combustion of methane, an attempt for correlating between activity, structure and surface properties.

2. Experimental

2.1. Catalysts preparation

$\text{La}_2\text{CuNiO}_6$ and LaNiO_3 were prepared by the sol–gel method. Stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in de-ionized water, then a certain amount of citric acid was added to form citric acid chelate compounds. The solution was thickened at 70 °C under vigorous stirring to form a viscous gel and then was dried at 100 °C for 24 hours. The

* Corresponding author. Tel.: +86 471 4992982; fax: +86 471 4992981.
E-mail address: cehrs@imu.edu.cn (R. Hu).

xerogel was decomposed at 500 °C for 3 hours and finally calcined in a muffle furnace at 1100 °C in air for 3 hours to form the double perovskite $\text{La}_2\text{CuNiO}_6$ catalyst designated as sample 1#. For comparison, a single perovskite LaNiO_3 was synthesized with the same procedure, and was named as sample 2#.

2.2. Catalyst characterizations

The X-ray diffraction patterns were recorded with a D8 ADVANCE diffractometer (Bruker, Germany) using $\text{CuK}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$, 36 kV, 20 mA, scanning step = $2^\circ/\text{min}$). TPR was conducted with a TP-5000 multiple adsorption instrument (Xianquan, China). It was performed at a rate of $10^\circ \text{C min}^{-1}$ from room temperature up to 900 °C in a flow of 5% H_2/N_2 . XPS was performed on an AMICUS spectrometer (KRATOS, England). Binding energies were referenced to C1s at 284.6 eV. Magnetization was conducted with a LakeShore 7407 vibrating sample magnetometer (LakeShore, America) at $295 \pm 0.1 \text{ K}$, with a precision 10^{-7} Am^2 .

2.3. Catalyst evaluation

The reaction of methane was carried out in a conventional flow system under atmospheric pressure. 200 mg catalyst (40–60 mesh) was loaded in a fixed bed quartz reactor (i.d. 10 mm). The reaction gas composition is $\text{CH}_4:\text{O}_2:\text{N}_2 = 2:18:80$, controlled by mass flow controllers at space velocity of 48,000 l/h. The inlet and outlet gas compositions were analyzed by an online gas chromatography (GC-2014C, Japan) with a packed column of carbon molecular sieve and a thermal conductivity detector.

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD patterns of the two catalysts are shown in Fig. 1. It can be seen that the sample 1# has diffraction peaks at $2\theta = 23^\circ, 32^\circ, 40^\circ, 46^\circ, 58^\circ$ and 68° , which are typical perovskite diffraction peaks. No other peaks were observed. Compared with the sample 2#, some shift of the diffraction peaks occurred. It can be assured from the diffraction peaks and literature data [12] that the sample 1# formed single-phase $\text{La}_2\text{CuNiO}_6$. In addition, narrow and intensive high diffraction peaks of the sample 1# indicated a well crystallized structure. The XRD patterns of sample 2# have good agreement with the standard LaNiO_3 . No additional peaks were observed. It indicates that

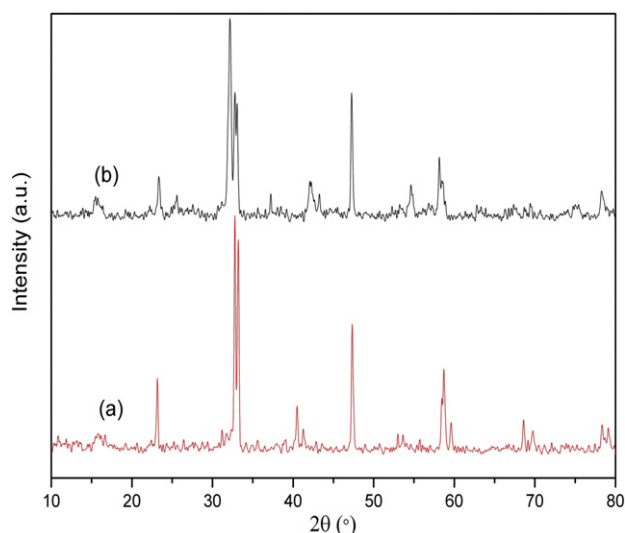


Fig. 1. XRD patterns of (a) $\text{La}_2\text{CuNiO}_6$ and (b) LaNiO_3 .

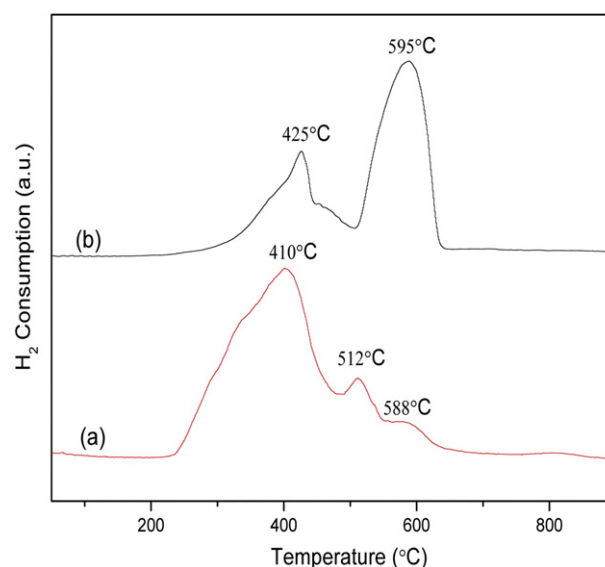


Fig. 2. H_2 -TPR profiles of (a) $\text{La}_2\text{CuNiO}_6$ and (b) LaNiO_3 .

sample 2# is a single phase LaNiO_3 . In perovskite structure, when the structure is non-ideal, t (Goldschmidt tolerant factor) is used to represent the deviation. When $t = 1$, the corresponding structure is an ideal perovskite structure. When $0.75 < t < 1$, ABO_3 stable perovskites could be formed with hexagonal, cubic, or orthorhombic structures according to different ion radius [13]. The tolerance factor, crystallite and lattice constants of catalysts are shown in Table 1. From the crystallite and lattice constants we can see that both catalysts have hexagonal crystal structures, deviated from the ideal cubic crystal.

3.2. H_2 -TPR analysis

Temperature-programmed reduction profiles were performed with the aim to study the reducibility of the prepared perovskites (Fig. 2). Typically, the LaNiO_3 has two peaks at 420 °C and 580 °C, corresponding to $\text{Ni}^{3+} \rightarrow \text{Ni}^{2+}$ and $\text{Ni}^{2+} \rightarrow \text{Ni}^0$ reduction respectively [14]. The CuO has two peaks at 350 °C and 500 °C which can be assigned to the reduction of $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ and $\text{Cu}^+ \rightarrow \text{Cu}^0$ respectively [15]. H_2 -TPR profiles of $\text{La}_2\text{CuNiO}_6$ catalyst exhibits three hydrogen consumption peaks. The first H_2 consumption peak, centered at 410 °C, is due to the overlapping reduction of Cu^{2+} to Cu^+ and Ni^{3+} to Ni^{2+} . The peaks at 512 °C and 588 °C are probably to the further reduction of Cu^+ to Cu^0 and Ni^{2+} to Ni^0 respectively. It can be seen from Fig. 2 that the reduction temperature of sample 1# is lower than that of sample 2# and peak area for sample 1# is larger than that for sample 2#, suggesting that sample 1# can provide more active oxygen species available for the oxidation reaction, which is in accord with the methane catalytic combustion activity.

3.3. XPS analysis

The surface chemical species of the catalysts were characterized by XPS and the results are summarized in Table 2. The O1s spectra in

Table 1
Tolerance factor, crystallite and lattice constants of catalysts.

Catalysts	Phase ^a	Crystallite (nm) ^a	Tolerance factor ^b	Lattice parameter ^a s					
				a/Å	b/Å	c/Å	α	β	γ
1#	$\text{La}_2\text{CuNiO}_6$	48.1	0.825	5.50	5.50	13.33	90°	90°	120°
2#	LaNiO_3	65.8	0.833	5.47	5.47	6.60	90°	90°	120°

^a Phase, crystallite, lattice parameters obtained by XRD analysis.

^b Tolerance factor obtained by calculation.

Download English Version:

<https://daneshyari.com/en/article/50673>

Download Persian Version:

<https://daneshyari.com/article/50673>

[Daneshyari.com](https://daneshyari.com)