

Methane oxidation by lattice oxygen of $\text{CeNbO}_{4+\delta}$

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Abstract

The reactivity of methane with lattice oxygen of cerium niobate, $\text{CeNbO}_{4+\delta}$, was studied by temperature-programmed reduction (TPR) in dry CH_4 flow at 523–1073 K. Phase transformations and reduction of cerium niobate at 900–1023 K lead to a massive release of hyperstoichiometric oxygen, in amounts determined by the intermediate-temperature phase composition dependent on thermal history. In this temperature range, CH_4 -TPR shows prevailing formation of carbon monoxide and steam, suggesting that the synthesis gas generation occurs in parallel with extensive oxidation of H_2 on the cerium niobate surface. At 1073 K when $\delta \rightarrow 0$, the reaction of methane with $\text{CeNbO}_{4+\delta}$ selectively yields synthesis gas with H_2/CO ratio close to two.

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1. Introduction

Ceria-based oxide materials are widely used as catalysts for carbon monoxide and hydrocarbon oxidation, SO_x reduction, water–gas shift and (de)hydrogenation reactions, liquid waste treatment by catalytic wet oxidation, and as key components of the three-way catalysts for automotive exhaust emission control [1–4]. Recently, significant attention was focused on the use of ceria and its derivatives for the partial oxidation of methane to synthesis gas (syngas) [5–12]. This mixture of hydrogen and carbon monoxide is an important feedstock for the Fischer–Tropsch and methanol syntheses. The industrial production of syngas by steam reforming of methane is an energy- and capital cost-intensive process, and yields H_2/CO ratio (~ 3) higher than required for the Fischer–Tropsch reaction. On the contrary, the catalytic partial oxidation of methane (POM) is mildly exothermic ($\text{CH}_4 + 1/2\text{O}_2 = \text{CO} + 2\text{H}_2$, $\Delta H_{298}^0 = -36$ kJ/mol) and gives the H_2/CO ratio of 2, favorable

for subsequent synthesis [13]. In addition to a significant catalytic activity towards POM, the advantages of ceria-based catalysts include the suppression of carbon deposition and stabilization of highly dispersed metal particles [1,2,5–7]. Furthermore, the use of $\text{CeO}_{2-\delta}$ and its derivatives makes it possible to generate synthesis gas in redox cycles when methane reacts with the lattice oxygen of ceria in the absence of gaseous O_2 , forming hydrogen and carbon monoxide at the first step; then $\text{CeO}_{2-\delta}$ is re-oxidized by air, steam or CO_2 during the second step of the cycle [14,15].

The present work is focused on the evaluation of cerium niobate, $\text{CeNbO}_{4+\delta}$, for possible use in the natural gas conversion processes. This material is known to exhibit a wide range of oxygen hyperstoichiometry (δ) varying from 0 to 0.33. Below 1023 K in air, cerium niobate forms four distinct phases, namely $\text{CeNbO}_{4.00}$ (monoclinic fergusonite-type structure, space group $I2/a$), two partially-oxidized $\text{CeNbO}_{4.08}$ and $\text{CeNbO}_{4.25}$ monoclinic compounds with ordering leading to superstructures, and triclinic $\text{CeNbO}_{4.33}$ [16–18]. Any excess oxygen is expected to incorporate into interstitial positions, while the charge is

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balanced by changing cerium oxidation state from basic 3+ to 4+; the dominant oxidation state of niobium cations is 5+. Heating of $\text{CeNbO}_{4+\delta}$ above 1023 K in air results in a transition into tetragonal scheelite-type polymorph, having a mixed oxygen-ionic and p-type electronic conductivity [18–20]. On reduction, tetragonal $\text{CeNbO}_{4+\delta}$ becomes again monoclinic; at 1073 K this transformation occurs when the oxygen partial pressure is close to approximately 3×10^{-15} atm [20]. Notice that the crystal lattice instability characteristic of morphotropic phase transitions should have a positive effect on the catalytic activity due to weakening of metal-oxygen bonds [21]. Having all these aspects in mind, particular goals of this work were to study the variations of oxygen content in $\text{CeNbO}_{4+\delta}$ in the course of redox cycling, and to assess the reactivity of lattice oxygen with methane.

2. Experimental

Samples of $\text{CeNbO}_{4+\delta}$ were prepared via standard solid-state reaction from stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich 99%) and Nb_2O_5 (Aldrich 99.99%). After thermal decomposition of nitrate, the oxide mixture was heated in air at 1273 K for 12 h, ball-milled, and then fired at 1673 K during 16 h. The product was subsequently ball-milled and pressed into pellets at 300 MPa. Dense ceramic samples were sintered in air at 1873 K for 5 h. As the conventional synthesis of cerium niobate requires prolonged treatment at high temperatures [17,18], the powdered samples for X-ray diffraction (XRD), thermogravimetric (TGA) and temperature programmed reduction (TPR) analyses were obtained regrinding dense ceramics; the specific surface area of the resulting powder was $0.73 \text{ m}^2/\text{g}$. All $\text{CeNbO}_{4+\delta}$ samples were equilibrated with air at 1373 K for 2 h and then cooled down to room temperature at different rates.

The room-temperature XRD patterns were collected using a Rigaku D/MAX-B diffractometer ($\text{Cu K}\alpha$ radiation, $2\theta = 10\text{--}80^\circ$, step 0.02° , 1 s/step). The thermal expansion was studied in one Linseis L75 alumina dilatometer at 298–1373 K, in air, with heating/cooling rate of 3–10 K/min. Thermogravimetric analysis was performed using a Setaram SetSys 16/18 instrument in a flow of dried air or 10% H_2 –90% N_2 gas mixture (2 l/h) in the temperature range of 298–1273 K. As illustrated in the inset of Fig. 1, the TGA procedure included two temperature cycles in air (heating: 10 K/min; cooling: 2 K/min), and heating in 10% H_2 –90% N_2 mixture (10 K/min). Then the sample was reduced in flowing 10% H_2 –90% N_2 mixture at 1273 K for 10 h in order to estimate the absolute oxygen content.

CH_4 -TPR was carried out at 523–1073 K on heating with a rate of 10 K/min using an U-shape quartz fixed-bed reactor (inner diameter of 3 mm, methane flow rate of $22.4 \text{ cm}^3/\text{min}$ STP, sample weight of 0.4 g). The sample used for CH_4 -TPR was initially equilibrated with air at 1373 K and cooled to room temperature at 5 K/min. After the first CH_4 -TPR run, the reactor was flushed with

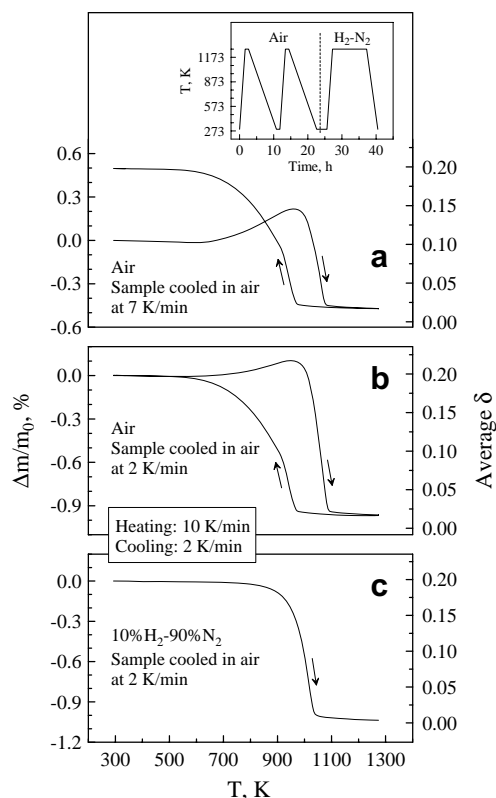


Fig. 1. Relative weight changes and average oxygen hyperstoichiometry of $\text{CeNbO}_{4+\delta}$ on heating and cooling in flowing air (a and b), and in 10% H_2 –90% N_2 mixture (c). Inset shows the temperature profile of TGA procedure.

helium; the sample was re-oxidized in oxygen flow at 1073 K for 0.5 h and cooled in gaseous O_2 down to room temperature (7 K/min). Then the CH_4 -TPR run was repeated. The composition of the effluent gas mixture was analyzed by a QMS200 mass spectrometer (Stanford Equipment). The rate of reaction product formation (W , mol/sec) was calculated from the corresponding concentration and total flow rate at the reactor outlet; the relative error was lower than 5% with respect to the maximum W values for a given product. In the course of experiments, no carbon imbalance between the influent and effluent gas flows was detected within the sensitivity limits of mass-spectrometric analysis. This shows that amount of deposited carbon, if any, was lower than 0.005% with respect to the sample weight.

3. Results and discussion

CH_4 -TPR showed that extensive oxidation of methane over the surface of $\text{CeNbO}_{4+\delta}$ starts at 700–750 K and has a maximum rate at 920–960 K (Fig. 2). This behavior is clearly related to the losses of lattice oxygen, accompanying phase changes. According to XRD data, $\text{CeNbO}_{4+\delta}$ furnace-cooled in air is a phase mixture comprising $\text{CeNbO}_{4.00}$, $\text{CeNbO}_{4.08}$ and $\text{CeNbO}_{4.25}$; the relative fractions of these phases are strongly dependent on the thermal

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