CO Catalytic Oxidation of Pt-Loaded Perovskite BaTiO₃ Near Ferroelectric-Phase Transition Temperature

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Abstract

Perovskite BaTiO₃ (BTO) nanocrystals with a size of 150–200 nm have successfully been synthesized via a facile hydrothermal method by employing titanate nanowires as synthetic precursor. Tetragonality and spontaneous ferroelectric polarization of BTO nanocrystals have been determined by X-ray diffraction and transmission electron microscopy investigations. BTO nanocrystals loaded with Pt nanoparticles in a size of 2–5 nm have been explored as a catalyst towards CO oxidation to CO₂. It is interesting to find that CO catalytic conversion rate over Pt-BTO nanocrystals gradually decreased and further increased near 100 °C when the catalytic temperature keeps increasing, whereas the conversion behavior in oxides is expected to be enhanced upon the catalytic temperature grows. Using differential scanning calorimetry and first-principle calculations, the observed catalytic behavior has been discussed on the basis of the ferroelectric polarization effect and the ferroelectric–paraelectric transition of BTO nanocrystals with a Curie temperature of ~ 110 °C. Below Curie temperature, CO catalytic oxidation could be significantly tailored by ferroelectric polarization of BTO nanocrystals via a promoted dissociation of O₂ molecules. The findings suggest that a ferroelectric polarization in perovskite oxides could be an alternative way to modify the CO catalytic oxidation.

Keywords Perovskite · Ferroelectric materials · BaTiO₃ · Pt · Catalysis

1 Introduction

In the past decades, numerous function oxide nanomaterials have been the focus of extensive investigations because of their fruitful chemical compositions and fascinating physical and chemical properties, affording potential applications in electronic devices [1–6], and various catalytic systems [7–10]. In particular, ferroelectric perovskite oxides, characterized by a switchable electric polarization, have been revealed to demonstrate a fascinating surface

chemistry and strong interaction with different gas and organic molecules, allowing us to further explore their catalytic functionality [6, 11].

It has been experimentally reported that polarization direction and charged surface have a significant effect on the deposition of metal, pollutant degradation, and hydrogen generation of water splitting of ferroelectric-based photocatalytic materials, including BaTiO₃ and PbTiO₃ [12–16]. More interestingly, CO, NO_x, and CO₂ molecules have theoretically been predicted to show a ferroelectric polarization-dependent-binding energy, geometries and dissociation energies, offering a great guidance to design ferroelectric-based catalytic systems for polluted and greenhouse gas treatment [3, 17, 18]. For CO oxidation, a prominent work demonstrated a polarization-dependent activation energy from 96 kJ/mol (positive polarization surface) to 128 kJ/mol in Pd-loaded LiNbO₃ single crystals [19]. Nevertheless, such large-size ferroelectric single crystals are very expensive and their catalytic temperature for CO oxidation remains very high (in the range of 493–673 K), and as a comparison, single-crystal

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nanostructures of perovskite ferroelectric oxides are desired objects to address and understand the polarization effect on CO oxidation for possible practical application. Therefore, developing a low-cost and facile method to prepare faceted ferroelectric nanostructures in non-lead perovskite oxides system would be both of fundamental and practical interests to further explore and illustrate the impact of ferroelectric property on CO catalytic oxidation reaction.

In our previous work, Pt-loaded PbTiO_3 (PTO) nanostructures have systematically been investigated towards CO oxidation, and especially a selective deposition of Pt nanoparticles on the negative $\{111\}$ of PTO and the crystal-facet-dependent activation energies were identified [20–22]. Despite of much effort on polarization direction or crystal-shape-dependent catalytic activation, it remains unclear how the CO-oxidation conversion evolves as a development or disappearance of the ferroelectric polarization, such as below or above the Curie temperature, which is critical to identify the role of ferroelectric polarization in CO oxidation. To address this issue, ferroelectric perovskite oxide with a relatively low Curie temperature is preferred. Compared to those of perovskite PTO (763 K) [23] and LiNbO_3 (593 K) [24], we choose perovskite BTO to address this issue because of its low ferroelectric-phase transition temperature at $\sim 120^\circ\text{C}$ in bulk form.

In this work, we report for the successful preparation of perovskite BTO with uniform size via hydrothermal reaction using synthetic precursor of titanate nanowires as reactant. In addition, the Pt nanocrystals were dispersed on the surface of perovskite BTO by wet-chemical reaction. Moreover, the relation between perovskite BTO ferroelectric transition and the CO catalytic oxidation has been investigated, based on which a mechanism for ferroelectric tailored CO catalytic oxidation is proposed and illustrated in detail.

2 Experimental

2.1 Synthesis

Tetragonal perovskite BaTiO_3 (BTO) was prepared via a facile hydrothermal method by employing $\text{K}_2\text{Ti}_6\text{O}_{13}$ nanowires as synthetic reactant and template. Briefly, the hydrothermally obtained $\text{K}_2\text{Ti}_6\text{O}_{13}$ nanowires [25] and analytical grade $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ were used as the starting substance (Ti/Ba molar ratio is 1.25). Analytical grade NaOH (7 M) was employed as mineralizer. The hydrothermal treatment was performed in an autoclave at 200°C for 12 h. The resultant products were filtered and washed with 1% HNO_3 , deionized water, ethanol, and

subsequently dried at 60°C in air for further characterization.

The Pt/BTO nanocrystals were obtained by adding 0.05 M chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, aq) into the solutions containing well-dispersed BTO nanocrystals mentioned above. After stirring for 15 min at room temperature, 0.2 M sodium borohydride (NaBH_4 , reductant) solution was added dropwise into the mixture and then kept in the ultrasonic bath for 30 min. The final powder was derived after centrifuging, washing, and then drying at 60°C for 24 h.

2.2 Characterization

The as-synthesized samples were systematically investigated and characterized by X-ray diffraction (XRD, ARLXTRA, Thermo, Switzerland, CuK_α), scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan), and transmission electron microscopy (TEM, F20 using an accelerating voltage of 200 kV, FEI, America). High-resolution scanning transmission electron microscopy (STEM) imaging was carried out on an aberration-corrected HAADF-STEM (FEI Titan G2 80-200 Chemi STEM at 300 kV). Thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis was carried out on a TGA-SDT (Q600 V8.2 Build 100) instrument to investigate the phase transition temperature of the samples.

2.3 Catalysis

The ambient pressure CO oxidation and kinetic study was performed in a continuous flow fixed-bed quartz tubular reactor (6 mm i.d.). 50 mg (40–60 mesh) 1% Pt/BTO catalyst was packed in the reactor and pre-treated at 80°C for 2 h under a 50 ml/min dry He flow. After cooling to room temperature, a dry $\text{CO}/\text{O}_2/\text{He}$ mixture feeding stock was introduced into the reactor with different ratios and SVs. All reactants and products were analyzed by online gas chromatography.

2.4 Theoretical Calculation

Our first-principle calculations are carried out within the framework of density functional theory (DFT) using the VASP package [26]. DFT calculations were performed with a plane-wave basis (400 eV for the kinetic energy cutoff) and projector augmented wave potentials [27]. In the calculation, the generalized gradient approximation (GGA) in Perdew–Burke–Ernzerhof (PBE) format [28] was included. The external electric field was simulated by a periodic saw-tooth-like electrostatic potential [29] and the “positive” direction of the field refers to the direction pointing from oxygen molecule to substrate. The Pt surface

was modeled with a large supercell (6×6) approach by periodically repeated slabs. Each supercell contains four atomic layers of platinum plus the adsorbed molecule and a 20 Å-thick vacuum region. During the optimizations, the uppermost two platinum layers as well as the adsorbed molecule were allowed to relax until atom forces below 0.03 eV/Å. The Brillouin zone integration was performed with a single gamma point for geometric optimization.

3 Results and Discussion

Figure 1a, b presents the corresponding XRD patterns of the product hydrothermally prepared using synthetic reactant as titanate source [20]. All the diffraction peaks in Fig. 1a can be indexed into a tetragonal perovskite structure of BTO (JCPDS: 05-0626) with lattice constants of $a = 3.994$ Å, and $c = 4.038$ Å. The strong-and-sharp diffraction peaks imply a good crystalline nature of the as-synthesized sample. In particular, Fig. 1b gives the corresponding diffraction peaks within range 43° – 58° from Fig. 1a, and a remarkable splitting of diffraction peaks at

(002)/(200), (102)/(201), and (112)/(211) can be clearly observed, further identifying that the as-synthesized perovskite BTO adopts an obvious tetragonality perovskite phase and thus a possible spontaneous ferroelectric polarization [30]. Figure 1c, d presents the typical SEM images of the as-synthesized product in both low and high magnification. The as-synthesized BTO nanocrystals has been characterized to be 150–200 nm in size and formed with an aggregation of smaller particles to show an irregular morphology.

Moreover, TEM and Cs-corrected STEM were further performed to characterize the microstructure of the as-prepared perovskite BTO nanocrystals. As shown in Fig. 2, the as-prepared BTO crystals are in a size range of 150–200 nm, agreeing well with the SEM images in Fig. 1c, d. The STEM image in Fig. 2b indicates that BTO nanocrystals should be a typical single-crystal and the lattice fringes were calculated to be 3.993 Å and 4.028 Å, respectively, which match well with that of (100) and (001) lattice of tetragonal perovskite BTO (JCPDS: 05-0626). Accordingly, a tetragonality of BTO nanocrystals can be determined to be ~ 1.008 (c/a). In particular, an obvious

Fig. 1 **a** XRD pattern, **b** the magnification and indexation of three peaks within 42° – 58° , **c**, **d** SEM images of BTO product hydrothermally synthesized at 200 °C for 12 h

Fig. 2 **a** TEM (inset: magnified TEM image) **b** Cs-corrected STEM images of product hydrothermally synthesized at 200 °C, 12 h. (Ba: red dots; Ti: blue dots)

displacement of Ti atoms (blue dots) along the *c* axis (as indicated by the green arrow) in the tetragonal lattice of perovskite BTO can be observed compared to those of Ba atom positions (red circle). Such displacement provides a solid evidence to confirm an existence of a spontaneous ferroelectric polarization (*P_s*) in the as-prepared perovskite BTO. In addition, the direction of the *P_s* can be determined in Fig. 2b by considering Ti displacement. The above results clearly support that the as-synthesized BTO nanocrystals adopt a typical tetragonal and ferroelectric property, which are desirable for further CO catalytic oxidation experiment.

To investigate the effect of ferroelectric-phase transition on CO catalytic property, the Pt nanoparticles were synthesized on the tetragonal perovskite BTO surface by the reduction of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ from aqueous solution in a wet-chemical route. Figure 3 presents a typical high-resolution TEM (HRTEM) image of Pt-loaded perovskite BTO nanocrystals. As in Fig. 3, it can be observed that the Pt nanoparticles were uniformly dispersed on the surface of tetragonal perovskite BTO. The HRTEM image of a specific Pt nanoparticle on BTO surface shows clear crystal lattice with a uniform interplanar spacing of ~ 1.97 Å, corresponding to the (200) plane of cubic Pt (JCPDS 04-0802).

Figure 4 shows the CO catalytic behavior over Pt-BTO nanocrystals. The CO conversion rate was denoted as the CO_2 volume percentage content in the resultant products of the CO catalytic oxidation reaction system. It is fascinating to find that CO catalytic conversion behavior over Pt-BTO nanocrystals gradually decreased from 2.7% to 1.9% and further increased near 100 °C during the catalytic

Fig. 3 HRTEM image of Pt nanoparticles on the surface of perovskite BTO nanocrystal

temperature increased. This is the first time to observe that the catalytic activity of CO oxidation significantly decreased as the reaction temperature grew, which is very different from the conventional behavior of CO oxidation in typical TiO_2 and non-ferroelectric perovskite oxides [31, 32], where the catalytic activity of CO oxidation increased upon the catalytic temperature grows. In addition, CO oxidation activity of Pt-PTO nanocrystals in our previous work was also demonstrated to be significantly enhanced rather than lowered when the temperature was increased and far from a ferroelectric transition

Fig. 4 CO catalytic conversion rate on Pt-BTO nanocrystals. Conversion rate was referred to the volume percentage of CO₂ in the catalytic reaction gas flow

temperature. The interesting findings in Fig. 4 allow us to further consider the effect of the ferroelectric polarization on CO oxidation reaction. To address this issue, we attempted to determine the ferroelectric transition

temperature using DSC method. Figure 5a shows the differential scanning calorimetry of the as-synthesized perovskite BTO nanocrystals, from which it can be clearly observed that a ferroelectric-phase transition occurred at the temperature of about 108 °C, corresponding to a phase transition from tetragonal to cubic perovskite of the BTO nanocrystals [30], where the ferroelectric polarization disappeared near this transition temperature. Clearly, the ferroelectric transition temperature in Fig. 5a is very close to the temperature where the CO conversion rate over Pt-BTO changed drastically, as shown in Fig. 4. This could be understood simply by a proposition that below the Curie temperature, Ps could have played a crucial role in affecting the activity of CO oxidation, and the temperature effect becomes dominated when the ferroelectric polarization disappears above the Curie temperature, similar to those conventional oxides [33, 34].

It has been discussed previously that the kinetic orders of CO and O₂ over the Pt/PTO nanoplates, nanocrystals, and nanofibers are calculated to be apparently different from those monofunctional pathways that either have a $\sim [\text{O}_2]^1$ dependence over Pt [35], Pd [36] and Rh [37] catalysts through a $\ast\text{-CO}\ast$ -assisted O₂ activation as the

Fig. 5 **a** DSC curve of as-synthesized perovskite BTO nanocrystals, **b** bond length in the O₂ molecule adsorbed on Pt surface as a function of the applied electric field, **c** the structural model used for predicting the electric-field-dependent O₂ bond length

rate-determining step (rds) [37, 38] or a $\sim[\text{CO}]^{-1}$ dependence for CO desorption-controlled kinetics [39]. The reaction orders are close to the observed ones in a Pt/Rh/CeO₂/Al₂O₃ system involving a bifunctional pathway, which refers to a reaction between CO adsorbed on the metal and oxygen from near the metal/support interface [40]. This implies that the O₂ dissociative chemisorption near the Pt/BTO interface is the rds. For such rds, the bond length of O₂ molecules was critical for dissociative chemisorption and was predicted to be polarization-dependent, as shown in Fig. 5b. A structural model is used for predicting the electric-field-dependent O₂ bond length, as shown in Fig. 5c. Due to the O₂ dissociation site near the interface, the electric field is applied from Pt to BTO, corresponding to a negative polar surface of BTO. It can be observed that the bond length in the O₂ molecule is elongated largely from 1.398 to 1.408 Å when embedded in a positive electric-field effect, which is highly preferred for O₂ dissociative chemisorption. Such surface potential could be achieved on the negative polar surface of perovskite BTO that is unscreened or incompletely screened. Our results in Fig. 5b agree well with the report in Pt/PTO system, where the O₂ dissociative chemisorption energy is the lowest on the negative surface in Pt/PTO system [17].

Accordingly, we argue that the observed CO catalytic conversion behavior over Pt-BTO nanocrystals is attributed to the decrease and disappearance of ferroelectric polarization near the Curie temperature, below which O₂ dissociative chemisorption near Pt/BTO interface could be significantly tailored by the ferroelectric polar surface potential of perovskite ferroelectric BTO nanocrystals.

4 Conclusion

In conclusion, this study manifests the significance of ferroelectric polarization arise from perovskite nanocrystals in modifying catalytic reactions. Remarkable change is observed by using Pt nanocrystals loaded perovskite BTO nanocrystals in the conversion process of CO. It is proposed that the surface potential of perovskite BTO nanocrystals derived from the ferroelectric polarization plays a key role in modifying the CO catalytic behavior by facilitating the O₂ dissociative adsorption, leading to the drastic conversion rate variation at the Curie temperature of ferroelectric support BTO nanocrystals. The findings present here offer an opportunity to extend applications of ferroelectric nanomaterials into catalytic field, such as the oxidation of CO, NO_x, and organic synthesis. In addition, interface engineering and ferroelectric polarization controlling would be promising approaches to tailoring surface activity and optimize catalytic performance of ferroelectric-supported metal catalysts.

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