前驱体 CeOHCO_3 的结构对 CeO_2 催化性能的影响孙明娟^{1,2}, 邹国军¹, 许 珊¹, 王晓来^{1,*}¹中国科学院兰州化学物理研究所羰基合成与选择性氧化国家重点实验室, 甘肃兰州 730000²中国科学院研究生院, 北京 100049

摘要: 以尿素替代水为溶剂, 采用改良的尿素水解法制备不同结构的 CeOHCO_3 和 CeO_2 , 并运用 N_2 吸附-脱附、X 射线衍射、 H_2 程序升温还原、 O_2 程序升温脱附、X 射线光电子能谱、扫描电镜及甲烷燃烧反应对 CeO_2 催化剂进行表征和催化性能测试。结果表明, CeO_2 催化性能和前驱体 CeOHCO_3 的晶相结构 (六方相或八面体相) 存在直接关系。与以八面体为前驱体制得的颗粒状 CeO_2 相比, 以六方相为前驱体制得的棒状 CeO_2 具有比表面积大、氧化还原能力强、表面氧空缺浓度高以及催化甲烷燃烧活性高的特点。

关键词: 六方相; 碱式碳酸铈; 氧化铈; 棒状结构; 甲烷燃烧

中图分类号: O643

文献标识码: A

收稿日期: 2012-04-02. 接受日期: 2012-05-03.

*通讯联系人. 电话: (0931)4968082; 传真: (0931)8277088; 电子信箱: xlwanglicp@yahoo.com.cn

本文的英文电子版(国际版)由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

Effect of Structure of CeOHCO_3 Precursor of CeO_2 on Its Catalytic PerformanceSUN Mingjuan^{1,2}, ZOU Guojun¹, XU Shan¹, WANG Xiaolai^{1,*}

¹State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China

²Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: A modified hydrothermal process method based on using urea instead of water as the solvent was used to prepare CeOHCO_3 . Pure CeOHCO_3 with a single crystalline structure was produced by varying the experimental conditions. CeO_2 particles obtained from these CeOHCO_3 precursors were tested for CH_4 oxidation. The temperatures for 90% methane conversion were 604 and 647 °C for CeO_2 catalysts obtained from hexagonal and orthorhombic CeOHCO_3 , respectively, indicating that the CeO_2 catalyst from hexagonal CeOHCO_3 ($\text{CeO}_2\text{-A}$) was more active than that from the orthorhombic form ($\text{CeO}_2\text{-D}$). The specific surface area and pore volume of $\text{CeO}_2\text{-A}$ were 45 m^2/g and 0.35 cm^3/g , respectively, which were higher than those of $\text{CeO}_2\text{-D}$. H_2 -TPR showed a much lower reduction temperature and enhanced reducibility with $\text{CeO}_2\text{-A}$. XPS and O_2 -TPD results demonstrated there were more oxygen vacancies on the surface of $\text{CeO}_2\text{-A}$ than on $\text{CeO}_2\text{-D}$, which implied increased oxygen mobility. The CeOHCO_3 -structure dependent activity was investigated and found to originate from the morphologies of the CeOHCO_3 precursors. Hexagonal CeOHCO_3 had a rod-like shape while orthorhombic CeOHCO_3 had a sphere-like morphology. After calcination, the obtained CeO_2 had the morphology of the precursor. The difference in morphology gave CeO_2 catalysts with different texture, structure, reducibility, and thus catalytic activity.

Key words: hexagonal; cerium hydroxide carbonate; cerium oxide; rod-like; methane oxidation

Received 2 April 2012. Accepted 3 May 2012.

*Corresponding author. Tel: +86-931-4968082; Fax: +86-931-8277088; E-mail: xlwanglicp@yahoo.com.cn

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

Rare earth oxides are versatile functional materials with a wide range of applications in optics, electrical device, in-

formation science, catalysis, magnetism, and medicine, which arise from their special 4f electronic structure [1–3].

Among the rare earth materials, CeO_2 and its precursor CeOHCO_3 have been extensively studied [4–9]. Cerium hydroxide carbonate powders are attracting increasingly more research interests because they are suitable precursors to CeO_2 and are also novel functional materials as black-light emission materials and nonlinear optical materials [4,9]. Cerium oxide has widespread applications in UV blocking, fuel cells, catalysts, polishing materials, gas sensors, and high temperature oxidation resistance materials [5–8] due to its high oxygen storage capacity (OSC) associated with its rich oxygen vacancies and excellent redox property.

Many methods including the sol-gel process [7], hydrothermal or solvothermal synthesis [2,10], sonochemical [11], microemulsion [12], precipitation [13], thermal decomposition [14], and template or surfactant-assisted processes [15] have been developed to synthesize CeO_2 materials. Among these technologies, the most effective and economical route is the hydrothermal method based on urea hydrolysis [9,10]. By varying the experimental conditions including reaction time, reaction temperature, and amount of urea, CeO_2 particles with different sizes and shapes are produced. Besides the development of a robust synthesis approach for a size/shape-controlled nanostructure, another important aspect is the investigation of CeO_2 structure, size and shape dependent properties. For example, size-tunable CeO_2 crystals fabricated from various wet chemical approaches showed that their UV absorption behavior was size dependent [5]. Similarly, a size dependent effect on the Raman spectra was observed by Sun et al. [15]. Mai et al. [16] prepared CeO_2 particles of different shapes and investigated the relationship between the OSC and surface structure associated with a specific CeO_2 crystalline shape. The highest OSC was shown by nanocubes, followed by nanorods and nanopolyhedra. Zhou et al. [8] synthesized CeO_2 with various nanostructures from a cerium oxylate precursor and found that the activity for CO oxidation was in the sequence of nanoparticles > nanopolyhedra > mesoporous. There are many reviews on size and morphology/shape dependent properties of CeO_2 nanoparticles, but there is little information on the relationship between the structure of the CeOHCO_3 precursor and the catalytic activity of the derived CeO_2 .

It is known that CeOHCO_3 has two different phases, i.e., hexagonal and orthorhombic phases. The latter is the stable phase [9]. The properties of the CeO_2 materials obtained from these two phases can be different. In this paper, we reported a modified urea hydrolysis method employing urea as solvent instead of water to synthesize CeOHCO_3 with different structures. The CeO_2 materials produced from these precursors were investigated for methane combustion, to establish the correlation between the structure of the

CeOHCO_3 precursor and the catalytic activity of the derived CeO_2 . The underlying reason for the structure-performance relationship was discussed.

1 Experimental

1.1 Synthesis of CeOHCO_3 and CeO_2

The CeOHCO_3 precursor was prepared by a modified urea hydrolysis described in reference [17]. In a typical experiment, 15 mmol cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 10 g urea (166 mmol) without the addition of distilled water were mixed in a 5 ml beaker. This was followed by heating at 90 °C in an oven for 1–2 h. After the mixture became a clear and transparent solution, the beaker was put into a Teflon bottle that was kept in a stainless steel autoclave. After sealing it tightly, the autoclave was placed in an oven followed by an increase in temperature to 150 °C (at a rate of 10 °C/min from room temperature). This was kept for 24 h under the autogenous pressure without stirring. After the autoclave was cooled to room temperature, the resulting dense solid was washed with distilled water and ethanol, and dried at 80 °C for 24 h. Finally, CeO_2 was obtained after calcining the powder at 700 °C in air for 2 h. A series of experiments were conducted by changing synthesis time (24 or 36 h), amount of urea (10 or 40 g) and synthesis temperature (130, 150 or 170 °C) in order to synthesize a sample with a single crystalline structure.

1.2 Characterization

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO X-ray diffractometer using $\text{Cu } K_\alpha$ radiation. Brunauer-Emmett-Teller (BET) surface area was measured on a Micromeritics ASAP-2010 apparatus. H_2 temperature-programmed reduction (H_2 -TPR) measurement was performed at a rate of 10 °C/min from room temperature to 850 °C in a flow of 5% H_2/Ar mixture (35 ml/min) after a treatment for 1 h in O_2 flow at 500 °C. O_2 temperature-programmed desorption (O_2 -TPD) was carried out in He flow (20 ml/min) from room temperature to 900 °C with 10 °C/min. X-ray photoelectron spectroscopy (XPS) was performed on a photoelectron spectrometer (VG ESCALAB 210) with a monochromatic X-ray $\text{Mg } K_\alpha$ ($h\nu = 1253.6$ eV) source. The morphology of the nanocrystals synthesized was determined on a JEOL JSM-6701F scanning electron microscopy (SEM).

The CH_4 oxidation reaction was carried out with 0.5 g (20–40 mesh) catalyst by feeding 100 ml/min of gas mixture (1% CH_4 , air as the balance). The reactants and products were analyzed by an online GC (PE, Autosystem XL)

equipped with a carbon molecular sieve (TDX-1) packed column and a thermal conductivity detector (TCD).

2 Results and discussion

Similar to the use of an aqueous solution, the products of urea hydrolysis are CO_2 and NH_3 , which get dissolved in water. The solubility of NH_3 in H_2O is higher than that of CO_2 , resulting in a higher concentration of OH^- in the solution than of CO_3^{2-} , which will favor the formation of Ce (III) basic carbonate (CeOHCO_3) [18]. This is shown in Scheme 1. In Scheme 1, 1 mmol urea reacts with 3 mmol H_2O with the generation of 1 mmol OH^- and 1 mmol CO_3^{2-} which will consume 1 mmol Ce^{3+} to produce 1 mmol CeOHCO_3 . In our case, 45 mmol H_2O and 15 mmol urea were consumed in order to ensure the complete precipitation of 15 mmol Ce^{3+} . The water of crystallization contained in 15 mmol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is 90 mmol, which was sufficient for the hydrolysis of urea and complete precipitation of Ce^{3+} . This was supported by the observation that the experimental yield of the final product was close to the nominal value.

Scheme 1. Main reactions taking place in solution.

Many experimental parameters such as synthesis time, synthesis temperature, and amount of urea were investigated and found to be crucial factors in determining the structure and composition of the product. Here, in order to investigate the influence of the CeOHCO_3 structure on the catalytic performance of CeO_2 , four products obtained under different experimental conditions (Table 1) were chosen and studied.

Table 1 Summary of the products obtained under different synthesis conditions

Sample	Preparation condition	Crystalline size of CeO_2 (nm)	Lattice parameter (nm)
$\text{CeO}_2\text{-A}$	10 g $\text{CO}(\text{NH}_2)_2$, 150 °C, 24 h	21.3	0.5400
$\text{CeO}_2\text{-B}$	10 g $\text{CO}(\text{NH}_2)_2$, 130 °C, 36 h	21.3	0.5403
$\text{CeO}_2\text{-C}$	40 g $\text{CO}(\text{NH}_2)_2$, 130 °C, 24 h	18.4	0.5400
$\text{CeO}_2\text{-D}$	10 g $\text{CO}(\text{NH}_2)_2$, 170 °C, 24 h	16.9	0.5412

2.1 XRD patterns of CeOHCO_3 and CeO_2

CeOHCO_3 is the product from urea hydrolysis and has been proved to exist as two phases, orthorhombic CeO-

HCO_3 and hexagonal CeOHCO_3 [9,10,18]. Figure 1 shows the XRD patterns of the samples before calcination. For samples $\text{CeO}_2\text{-A}$ and $\text{CeO}_2\text{-B}$, all the peaks could be indexed to hexagonal CeOHCO_3 (JCPDS 32–189) [17] while in the case of samples $\text{CeO}_2\text{-C}$ and $\text{CeO}_2\text{-D}$, the diffraction was due to orthorhombic CeOHCO_3 (JCPDS 41–13). Except for some minor CeO_2 in sample $\text{CeO}_2\text{-C}$, there was no evident diffraction of any impurities in all samples, demonstrating good purity of the products. This result showed that pure hexagonal or orthorhombic CeOHCO_3 can be synthesized by using the suitable preparation conditions. This conclusion seems to be in conflict with the common idea that orthorhombic CeOHCO_3 is the stable phase and it is difficult to get pure hexagonal CeOHCO_3 under mild conditions [9,18]. Taking the novel solvent used into account, the formation and stabilization of hexagonal CeOHCO_3 can be explained as follows. The replacement of water by urea markedly changed the local environment for crystal growth such as polarity, viscosity, softness, and the pH value, which can have significant effects on the solubility of the precipitates and thus the crystalline structure of the final crystals [18].

Fig. 1. XRD patterns of the precursors obtained under different conditions.

Besides a change in crystalline structure, it is also worth noting that there were obvious differences in the crystallinity degree of the CeOHCO_3 precursors, which was connected with the phase composition (see Fig. 1). When orthorhombic CeOHCO_3 was the only product, the degree of crystallinity was very high and subsequently large particles were formed. When pure hexagonal CeOHCO_3 appeared, small grains with poor crystallinity were obtained. The different degree of crystallinity in the two samples can be partially attributed to the different morphologies of orthorhombic and hexagonal CeOHCO_3 because products with different phase constitutions had distinct morphologies [19], which will be discussed later.

After calcination, the sample was crystallized and all the diffractions in Fig. 2 were those of CeO_2 with the fluorite crystal structure (JCPDS 81-0792) regardless of the crystalline structure of the precursor. From the Scherrer equation and the (111) diffraction peaks, the mean crystallite sizes of CeO_2 were found to be in the range of 17–21 nm (Table 1). Sample CeO_2 -A and CeO_2 -B possessed a larger size of 21 nm while a smaller size of 17 nm was found with sample CeO_2 -C and CeO_2 -D. From the combination of the XRD patterns of the precursor and CeO_2 (Figs. 1 and 2), a conclusion can be made that the change trend in particle size of CeO_2 was opposite to that of CeOHCO_3 . This was not sur-

prising considering the thermal behavior of CeOHCO_3 with different degrees of crystallinity, since the phase transformation from CeOHCO_3 to CeO_2 was not kinetically favored with large CeOHCO_3 and would result in CeO_2 with a small crystallite size, and vice versa [6]. The lattice parameter was determined to be $a \approx 0.5400$ for samples CeO_2 -A, CeO_2 -B, and CeO_2 -C, while it was 0.5412 for sample CeO_2 -D. As compared with the other samples, the increased lattice parameter in sample CeO_2 -D was largely due to the size effect [13]. Since our XPS results did not show an excess amount of oxygen vacancies, this excluded the possibility that the lattice expansion was induced by oxygen vacancies.

Fig. 2. XRD patterns of CeO_2 samples obtained under different conditions.

2.2 Catalytic performance

The catalytic activities of the CeO_2 catalysts as a function of reaction temperature were investigated. The results are presented in Fig. 3. Similar activities were displayed by samples CeO_2 -A and CeO_2 -B, which were much higher than those obtained from samples CeO_2 -C and CeO_2 -D. Sample CeO_2 -A showed the best performance while sample CeO_2 -D

Fig. 3. Conversion of CH_4 versus reaction temperature over different CeO_2 catalysts synthesized under different conditions.

was the worst among the tested samples. At 550 °C, CH_4 conversion was 58.7% over sample CeO_2 -A but it was only 42.4% over sample CeO_2 -D. The corresponding conversion rates of CH_4 were 6.00 and 4.38 mmol/(g·h). The conversion rate of CH_4 over sample CeO_2 -A was clearly higher than that over sample CeO_2 -D. The order of activity demonstrated that CeO_2 materials derived from hexagonal CeOHCO_3 were more active than those derived from orthorhombic CeOHCO_3 .

The catalytic results (Fig. 3) could not be explained by the XRD data (Fig. 1), because samples CeO_2 -C and CeO_2 -D had the smallest crystallite sizes but exhibited the lowest activity, which indicated that the crystallite size of CeO_2 was not the critical factor in determining the catalytic activity. On the other hand, it is generally acknowledged that the catalytic performance for methane combustion over ceria strongly depends on its surface area/pore volume and redox property [8,20,21]. High surface area catalytic materials exhibiting numerous crystal faces and corners, which are considered active sites for the adsorption of reactants, would give better catalytic performance [8]. Also, a facile reduction process between Ce^{4+} and Ce^{3+} is accepted as necessary for enhanced catalytic activity [20,21]. Therefore, in order to show the determining factor contributing to the

different activities of CeO_2 induced by the different structures of the CeOHCO_3 precursor, two samples (CeO_2 -A), and (CeO_2 -D) were further investigated by BET, H_2 -TPR, O_2 -TPD, XPS, and SEM measurements.

2.3 Specific surface area and pore structure

The nitrogen adsorption-desorption isotherms and pore size distributions of the CeO_2 samples are shown in Fig. 4. The textual properties are listed in Table 2. The isotherms of both CeO_2 -A and CeO_2 -D were of Type II (IUPAC classification) with the maximum pore size at 25 and 8 nm for CeO_2 -A and CeO_2 -D, respectively. The specific surface area of CeO_2 -A was $45 \text{ m}^2/\text{g}$ and the pore volume was $0.35 \text{ cm}^3/\text{g}$. The measured specific surface area for CeO_2 -D was $38 \text{ m}^2/\text{g}$ with a pore volume of $0.25 \text{ cm}^3/\text{g}$. The trend of the change in pore volume was identical to that of surface area, showing that the structure of the pore played an important role in determining the surface area of the sample. At high temperature, the catalytic combustion of CH_4 is limited by the mass transfer of reactants to the catalyst surface from the gas phase [22], and a high surface area and large pore structure are important for a faster reaction under mass transfer limitation.

2.4 Reducibility

Figure 5(a) presents H_2 -TPR profiles of the CeO_2 catalysts. The different structures in the precursors caused significant changes in the reduction behavior of the CeO_2 samples. Three consumption peaks, α peak ($100\text{--}280^\circ\text{C}$ and $300\text{--}430^\circ\text{C}$), β peak ($430\text{--}600^\circ\text{C}$), and γ peak ($> 600^\circ\text{C}$), were detected with CeO_2 -A [23]. In contrast, CeO_2 -D exhibited a broad reduction profile centered at 366°C and a high temperature reduction peak above 700°C . According to Ref. [24], peaks in the lower temperature region can be assigned

Table 2 Specific surface area and pore volume of the samples

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
CeO_2 -A	45	0.35	14.8
CeO_2 -D	38	0.25	11.5

to the reduction of surface Ce^{4+} to Ce^{3+} and the peaks at temperatures higher than 700°C can be attributed to the reduction of bulk CeO_2 . Compared with the H_2 -TPR profile of CeO_2 -D, the peak area below 600°C of CeO_2 -A was much larger and its H_2 uptake of $694 \mu\text{mol/g}$ was three times higher than that of CeO_2 -D ($180 \mu\text{mol/g}$), indicating a larger amount of active surface oxygen atoms. This observation was consistent with the trend of the specific surface area (Table 2). It was reported that the intensity of the low temperature peak was related to the surface area of the materials [25]. Here, CeO_2 -A with a higher specific surface area tended to have more crystal edges and corners, which in turn produced a higher concentration of surface oxygen species.

O_2 -TPD was also employed to determine the mobility of the oxygen species. The corresponding profiles are shown in Fig. 5(b). Only one desorption peak below 300°C , assigned to O_2^- formed by adsorbing O_2 at an oxygen vacancy by reaction [26], was observed for both samples. This peak represented active oxygen species that were correlated to catalytic activity for oxidation [20]. In contrast to CeO_2 -D, a shift towards lower temperature by 21°C was detected with CeO_2 -A, suggesting enhanced oxygen mobility in the latter. This was also in agreement with the decreased reduction temperature of the α peak in Fig. 5(a) (162°C for CeO_2 -A versus 366°C for CeO_2 -D). A much larger area appeared with CeO_2 -A, which was evidence of more chemically adsorbed oxygen species. Together with the increased oxygen mobility indicated by the decreased desorption temperature, more of the active oxygen promoted the redox change be-

Fig. 4. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of the CeO_2 samples.

Fig. 5. H_2 -TPR (a) and O_2 -TPD (b) profiles of CeO_2 samples.

tween Ce^{4+} and Ce^{3+} . Consequently, this was evidence of the superior redox property of CeO_2 -A. This was additional evidence for that the CeOHCO_3 structure modified the reduction behavior of CeO_2 materials, and the CeO_2 structure from hexagonal CeOHCO_3 gave excellent reducibility, as found by H_2 -TPR.

2.5 Surface structure

As reported in a previous study [9], hexagonal CeOHCO_3 is a metastable structure. For this reason, a large amount of defects may be present in hexagonal CeOHCO_3 , which would facilitate the migration of lattice oxygen from the bulk to the surface and thus enhance the catalytic rate. To confirm this, XPS measurement was conducted. The O 1s profiles at 524–535 eV are shown in Fig. 6. The profiles were fitted with two peaks, which were due to lattice oxygen O^{2-} (529–530 eV) and chemisorbed OH (531–533 eV) adsorbed on the vacancies or unsaturated chemical bonds on the surface [27]. The relative concentration of the chemisorbed OH groups with respect to total oxygen was calculated and found to be 0.34 in CeO_2 -A, while it was only 0.23 in CeO_2 -D. Obviously, CeO_2 -A possessed more oxygen vacancies on the surface than CeO_2 -D. Oxygen vacancies indicated active oxygen species generation and also increased mobility of oxygen in the bulk, which was in good agreement with the enhanced reducibility in CeO_2 -A shown in the H_2 -TPR and O_2 -TPD results.

Fig. 6. O 1s XPS spectra of CeO_2 samples.

2.6 Morphology

The morphologies of the CeOHCO_3 precursors and CeO_2 samples were examined by SEM. As seen from Figs. 7(a) and (b), hexagonal CeOHCO_3 displayed a rod-like morphology while orthorhombic CeOHCO_3 had a spherical shape. It is probably easier to agglomerate spherical crystals, and this would explain the large grains with good crystallization that were produced from orthorhombic CeOHCO_3 (shown in Fig. 1). After calcination, the shape of the CeOHCO_3 was maintained in the conversion to CeO_2 (Figs. 7(c) and (d)). A rod-like structure and a spherical morphology were detected in the CeO_2 particles derived from the hexagonal and orthorhombic CeOHCO_3 , respectively.

It was reported that the functional performance of CeO_2 materials were strongly influenced by their sizes and morphologies [2,18,28]. Based on the discussion in Section 2.2, the absence of a correlation between the catalytic activity and crystallite size excluded the possibility that the crystallite size of CeO_2 was the determining factor for activity. Therefore, the structure dependent performance of CeO_2 for CH_4 oxidation was considered to originate from the different morphologies of the CeOHCO_3 precursors. It is well known that the oxygen vacancy distribution and transformation of oxygen are closely related to the morphology, with one dimensional materials that have more oxygen vacancies being more advantageous for the storage and release of oxygen than zero dimensional materials. Indeed, in our case, H_2 -TPR and O_2 -TPD analyses confirmed that the CeO_2 material with the rod-like morphology derived from hexagonal CeOHCO_3 had enhanced mobility of lattice oxygen, increased the amount of reactive Ce^{4+} species and more facile reducibility. This means that the oxygen in rod-like crystals would be more easily attacked by CH_4 molecules, resulting in a lower complete oxidation temperature than that in CeO_2 particles produced from orthorhombic CeOHCO_3 . In addi-

Fig. 7. SEM images of CeOHCO_3 (a and b) and CeO_2 (c and d) samples prepared under different conditions. (a) and (c): 10 g $\text{CO}(\text{NH}_2)_2$, 150 °C, 24 h; (b) and (d): 10 g $\text{CO}(\text{NH}_2)_2$, 170 °C, 24 h.

tion, the high aspect ratio of the rod-like shape was helpful in preventing sintering under high temperature calcination, and hence CeO_2 with a high surface area and large pore volume was obtained (Table 2), which was more active for CH_4 oxidation.

3 Conclusions

A modified hydrolysis method was used to synthesize CeOHCO_3 with different crystalline structures. The catalytic activities of CeO_2 obtained from these for CH_4 oxidation were investigated and found to be structure dependent. The activity was in the order CeO_2 nanorods (hexagonal CeOHCO_3 as precursor) > CeO_2 nanoparticles (orthorhombic CeOHCO_3 as precursor). The higher activity of CeO_2 from hexagonal CeOHCO_3 was due to a large surface area, more facile reducibility and abundant oxygen vacancies on the surface. This work provided a method for designing better catalytic materials by the selection of synthesis parameters to obtain the hexagonal phase for the CeOHCO_3 precursor.

References

- Zhang Y J, Gao M R, Han K D, Fang Z Y, Yin X B, Xu Z Y. *J Alloys Compd*, 2009, **474**: 598
- Zhang D S, Niu F H, Yan T T, Shi L Y, Du X J, Fang J H. *Appl Surf Sci*, 2011, **257**: 10161
- 李斌, 李士杰, 王颖霞, 李能, 张婉静, 林炳雄. 催化学报 (Li B, Li Sh J, Wang Y X, Li N, Zhang W J, Lin B X. *Chin J Catal*), 2010, **31**: 528
- Zhao D L, Yang Q, Han Z H, Sun F Y, Tang K B, Yu F. *Solid State Sci*, 2008, **10**: 1028
- Mamontov E, Egami T, Brezny R, Koranne M, Tyagi S. *J Phys Chem B*, 2000, **104**: 11110
- Wang H C, Lu C H. *Mater Res Bull*, 2002, **37**: 783
- Bumajdad A, Eastoe J, Mathew A. *Adv Colloid Interface Sci*, 2009, **147-148**: 56
- Zhou H P, Zhang Y W, Si R, Zhang L S, Song W G, Yan C H. *J Phys Chem C*, 2008, **112**: 20366
- Han Z H, Guo N, Tang K B, Yu S H, Zhao H Q, Qian Y T. *J Cryst Growth*, 2000, **219**: 315
- Cui M Y, He J X, Lu N P, Zheng Y Y, Dong W J, Tang W H, Chen B Y, Li C R. *Mater Chem Phys*, 2010, **121**: 314
- Yu J C, Zhang L, Lin J. *J Colloid Interface Sci*, 2003, **260**: 240
- Pan C S, Zhang D S, Shi L Y. *J Solid State Chem*, 2008, **181**: 1298
- Li X D, Li J G, Huo D, Xiu Z M, Sun X D. *J Phys Chem C*, 2009, **113**: 1806
- Guo Z Y, Du F L, Cui Z L. *Mater Chem Phys*, 2009, **113**: 53
- Sun C W, Li H, Wang Z X, Chen L Q, Huang X J. *Chem Lett*, 2004, **33**: 662
- Mai H X, Sun L D, Zhang Y W, Si R, Feng W, Zhang H P, Liu H C, Yan C H. *J Phys Chem B*, 2005, **109**: 24380
- Sun M J, Zou G J, Xu S, Wang X L. *Mater Chem Phys*, 2012, **134**: 912
- Chen S F, Yu S H, Yu B, Ren L, Yao W T, Cölfen H. *Chem Eur J*, 2004, **10**: 3050

- 19 Fu C, Li R X, Tang Q, Li C Q, Yin S, Sato T. *Res Chem Inter-med*, 2011, **37**: 319
- 20 Qiao D S, Lu G Z, Mao D S, Guo Y, Guo Y L. *J Mater Sci*, 2011, **46**: 641
- 21 Zhou K B, Wang X, Sun X M, Peng Q, Li Y D. *J Catal*, 2005, **229**: 206
- 22 Li S Q, Wang X L. *Catal Commun*, 2007, **8**: 410
- 23 Miśta W, Malecka M A, Kępiński L. *Appl Catal A*, 2009, **368**: 71
- 24 单文娟, 刘畅, 郭红娟, 杨利华, 王晓楠, 冯兆池. 催化学报 (Shan W J, Liu Ch, Guo H J, Yang L H, Wang X N, Feng Zh Ch. *Chin J Catal*), 2011, **32**: 1336
- 25 Cabús-Llauradó M C, Cesteros Y, Medina F, Salagre P, Sueiras J E. *Microporous Mesoporous Mater*, 2007, **100**: 167
- 26 Liang Q, Wu X D, Weng D, Xu H B. *Catal Today*, 2008, **139**: 113
- 27 Ji P F, Zhang J L, Chen F, Anpo M. *J Phys Chem C*, 2008, **112**: 17809
- 28 Ho C, Yu J C, Kwong T, Mak A C, Lai S. *Chem Mater*, 2005, **17**: 4514