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Template-free and non-hydrothermal synthesis of CeO$_2$ nanosheets via a facile aqueous-phase precipitation route and catalytic oxidation properties

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ABSTRACT

Two types of CeO$_2$ nanosheets, petal-like and belt-like, were synthesized via a facile aqueous phase precipitation method and NH$_4$HCO$_3$ as precipitant at 0 °C and 25 °C, without hydrothermal or solvothermal treatment, without template or surfactant and without organic solvent. The reaction temperature and supersaturation played key roles in the formation of ceria nanosheets, namely, lower temperature and higher supersaturation were favorable to the synthesis of sheet-like CeO$_2$ by oriented aggregation of as-synthesized precursors nanocrystallines, whereas the elevated temperature could cause the dissolution-recrystallization of precursors and promote
the Ostwald ripening process, finally the polyhedral CeO$_2$ could be obtained through the thermal decomposition of precursors. Catalytic oxidation properties were investigated via catalytic oxidation of CO over CeO$_2$ and catalytic combustion of 1, 2-dichloroethane over VO$_x$/CeO$_2$. Compared with traditional CeO$_2$ nanoparticles, the ceria nanosheets showed more excellent catalytic oxidation activities.

**KEYWORDS:** CeO$_2$, nanosheets, catalytic oxidation, carbon monoxide, 1, 2-dichloroethane, vanadia

1. INTRODUCTION

Ceria has been widely used in catalysis, solid oxide fuel cells, oxygen sensors, ultraviolet blockers and chemical mechanical planarization processes, thus attracted tremendous attention. Over last years, remarkable progresses have been made in the synthesis of CeO$_2$ nanomaterials with various morphologies, such as nanorods [1], nanowires [2], nanotubes [3], nanoshuttles [4], nanoflowers [5] and other morphologies [6, 7], and in the investigation of their corresponding novel properties. Since the graphene was discovered in 2004 [8] and awarded the Nobel Prize in Physics in 2010, much more consideration has been given to synthesize metal oxides with two-dimensional (2D) nanostructures (such as nanoplates, nanodisks, nanoprisms, nanowalls, nanobelts and nanosheets) and investigate their novel applications, due to their unusual properties derived from exceptionally small thickness and possible quantum size effects [9]. However, it is difficult to synthesize 2D nanomaterials in
solution-phase, especially the material with face centered cubic structure (for example \( \text{CeO}_2 \)) because there is no intrinsic driving force to form anisotropic morphology. Therefore, few previous publications have reported the synthesis of 2D \( \text{CeO}_2 \), especially \( \text{CeO}_2 \) nanosheets.

Generally, \( \text{CeO}_2 \) nanosheets are synthesized under hydrothermal or solvothermal condition and these protocols usually require templates and surfactants or the specifical precursors such as \( \text{Ce(OH)CO}_3 \), and \( \text{Ce}_2(\text{CO}_3)_3 \), due to \( \text{CeO}_2 \) with the cubic structure. Li [10] reported the fabrication of \( \text{CeO}_2 \) nanosheets via controlling the morphology of \( \text{Ce(OH)CO}_3 \) precursors by a facile hydrothermal technique in the presence of hexamethylenetetramine (HMT) and acetic acid, and their results revealed that the amount of acetic acid was a key parameter for the nucleation and crystal growth of \( \text{Ce(OH)CO}_3 \) nanosheets. Yu [11] synthesized ultrathin mesoporous single-crystal-like \( \text{CeO}_2 \) nanosheets by a two-step hydrothermal treatment method. They firstly prepared Ce-EDA inorganic-organic hybrid nanorods via the hydrothermal reaction of \( \text{Ce(OAc)}_3 \) and 1,2-ethanediame (EDA) at 150 °C, and then the hybrid nanorods were further hydrothermally treated at 280 °C to form nanosheets. Deng [12] successfully synthesized platelet-like \( \text{CeO}_2 \) mesocrystals, constituted of 4-5 nm fused nanoparticles with interparticular voids along a common [002] axis through a benzyl alcohol-assisted solvothermal synthesis. Among these methods, the addition of templates, surfactants or organic solvent and high temperature were necessary. In recent years, without the assistance of any surfactant or template, \( \text{CeO}_2 \) nanosheets also were successively synthesized. For examples, Liu [13] synthesized \( \text{CeO}_2 \)
nanosheets with (110) dominated surface via a facile one step hydrothermal method (220 °C) and NH$_3$•H$_2$O was used to tailor the surface structure; Rao [14] described the preparation of mesoporous CeO$_2$ nanobelts by a hydrothermal route (120-140 °C) via only controlling cationic type (K$^+$, Na$^+$ or NH$_4^+$) and concentration of alkali, and the synthesized CeO$_2$ showed superior catalytic performance for CO oxidation; Sun [15] synthesized three-atom-thick ultrathin CeO$_2$ sheets with 20% surface pits at 180 °C via sodium oleate, CeCl$_3$ and NH$_3$•H$_2$O as starting materials. What was more, Yu [16] reported a simple, aqueous route to the synthesis of ultrathin, single-crystalline ceria nanosheets under non-hydrothermal condition of 95 °C, and the synthetic protocol involves the slow, continuous addition of cerium (III) nitrate into an aqueous solution containing 6-aminohexanoic acid (AHA). They found that the ceria nanosheets were formed through 2D self-organization of initially formed small ceria nanocrystals, followed by an in situ recrystallization process. Unfortunately, the template still was vital for their method. Besides, Minamidate [17], Han [18] and Wang [19] also reported the synthesis of plate-like ceria, monodisperse CeO$_2$ octahedra assembled by nanosheets and water-soluble Au-CeO$_2$ hybrid nanosheets by different methods. However, among reported methods, the requires of hydrothermal conditions (even the temperature up to 280 °C) or templates, surfactants or other organic additives, which made that the mechanism was not well understood and the post-treatment was difficult and complicated. Therefore, the synthesis of two-dimensional CeO$_2$ in a mild condition was still a great challenge.

Here we describe a simple, aqueous route to the synthesis of two-dimensional CeO$_2$
with petal and belt-like structure, without hydrothermal/solvothermal treatment, without templates and surfactants, without organic solvent and additive. Our simple synthetic protocol involves the quick addition of ammonium bicarbonate solution into cerium (III) nitrate solution at lower temperature (such as 0 °C and 25 °C). Moreover, catalytic activities of synthesized CeO$_2$ and VO$_x$/CeO$_2$ for the CO catalytic oxidation and 1, 2-dichloroethane catalytic combustion are investigated.

2. EXPERIMENTAL SECTION

2.1. Synthesis of CeO$_2$ nanosheets

In a typical synthesis procedure, 1.39 g cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$•6H$_2$O) and 0.75 g ammonium bicarbonate (NH$_4$HCO$_3$) were dissolved in 200 ml deionized water at 0 °C under magnetic stirring, respectively. After completely dissolved, the NH$_4$HCO$_3$ solution was poured rapidly into the Ce(NO$_3$)$_3$ solution, and then stirring for 0.5 h and statically aging 15 h at 0 °C. The final product was collected by filtration, washed with deionized water to remove any possible ionic remnants, and then dried at 110 °C and calcined at 450 °C for 4 h in air to prepare the petal-like CeO$_2$ nanosheet (labeled as CeO$_2$-0). To obtain different morphological CeO$_2$, the reaction/aging temperature and aging time were varied from 25 °C to 170 °C and 0 h to 48 h, respectively. Noting that, when the reaction/aging temperature was 75 °C and 100 °C, the reaction and aging processes were carried under reflux condition, and 150 °C and 170 °C were carried under hydrothermal condition. As reference, the CeO$_2$ particles (marked as CeO$_2$-TD) were prepared by the thermal
decomposition of Ce(NO$_3$)$_3$•6H$_2$O at 450 °C in air.

Vanadia was deposited on the ceria supports using incipient wetness of an aqueous solution of ammonium metavanadate (NH$_4$VO$_3$) and oxalic acid (C$_2$O$_4$H$_2$) in a 1:2 molar ratio. The concentration of vanadate and the amount of impregnation solution was adjusted in order to produce catalysts with 5 wt% vanadia weight loadings. After impregnation of the vanadate, the samples were dried overnight at 60 °C and then calcined in air at 450 °C for 4 h.

2.2. Characterization

The powder X-ray diffraction patterns (XRD) of samples were recorded on a Rigaku D/Max-rC powder diffractometer using Cu Ka radiation (40 kV and 100 mA). Scanning electron microscopy (SEM) experiments were performed on Hitachi S-3400N electron microscopes. The transmission electron microscope (TEM) images of the powder samples were recorded on a JEM-1400 instrument operated at 120 kV, and the high resolution TEM (HRTEM) images were recorded on a JEM-2100 instrument operated at 200 kV. The Fourier transform infrared spectroscopy (FT-IR) were obtained on a Nicolet 6700, and the samples were ground with KBr and pressed into thin wafer.

The H$_2$-TPR was performed in a quartz U-type tube quartz reactor using a TCD as detector. 100 mg sample was used and heated in O$_2$ at 450 °C for 1 h. Then the sample was cooled to 100 °C in O$_2$ flow (30 ml/min). The reducing gas was 5 vol.% H$_2$/Ar and its flow rate was 30 ml/min. The sample was heated at 10 °C/min from 100 to
750 °C. The CO$_2$-TPD was carried in the above equipment by an online MS (HIDEN HPR20), and the adsorption of CO$_2$ was performed at 100 °C.

### 2.3 Catalytic activity measurement

#### 2.3.1 Catalytic oxidation of CO

The catalytic activity of CeO$_2$ catalysts towards CO oxidation was carried out in a continuous flow reactor. The catalyst particles (200 mg) were placed in the reactor, and treated for 2 h in O$_2$ flow (10 ml/min) at 400 °C. The reactant gases (1.0% CO, 16% O$_2$, balanced with Ar) went through the reactor at a rate of 50 ml/min. The initial catalytic activity was continuously measured with the reaction temperature rising from 50 °C to 400 °C at 5 °C/min. The composition of the gas exiting the reactor was monitored by an online mass spectrometer (HIDEN HPR20).

#### 2.3.2 Catalytic oxidation of 1, 2-dichloroethane

Catalytic oxidation of 1, 2-dichloroethane was carried out with 200 mg of catalyst (40-60 mesh) in a continuous flow micro-reactor constituted of a U-shaped quartz tube of 3 mm of inner diameter at atmospheric pressure. The gas stream was composed of 450 ppm of 1, 2-dichloroethane and air in 50 cm$^3$/min (GHSV = 15,000 h$^{-1}$). The reaction was run from 100 to 250 °C in a step mode with a 15 min plateau at each temperature investigated. The effluent gases were analyzed by an on-line gas chromatograph equipped with a flame ionization detector (FID).
3. RESULTS AND DISCUSSION

3.1 Synthesis of CeO$_2$ nanosheets

The morphology of the final products synthesized at different temperatures (aging for 15 h) was observed by SEM (Figure 1a-f). As shown in Figure 1, when the reaction temperature was below 75 °C, the obtained products displayed obvious sheet-like morphology and the thickness of sheets was about 20-50 nm. However, some distinct differences among these nanosheets can still be observed. For instances, the nanosheets obtained at 0 °C were petal-like and self assembled into flower-like structure, by contrast, the product achieved at 25 °C was mainly consisted of uniform belt-like nanosheet with a length of about 5-10 µm and a width of about 0.5-1.2 µm. Additionally, the edges of belt-like nanosheets got rough and the shape also was non-uniform when the reaction temperature was increased to 50 °C. Further increasing the reaction temperature, the olive-like morphology was observed at 75 °C and 100 °C and composed by multilayer sheets. The magnified SEM images showed olive-like sheets were aggregated by CeO$_2$ nanoparticles. Be noted that, the sample obtained at 150 °C was prepared via a route of precipitation reaction at 100 °C and then hydrothermal treatment at 150 °C. Figure 1f demonstrated that the sample was mainly composed by irregular aggregated particles, however, the olive-like morphology can still be found (Figure S1). Therefore, it can be speculated that the dissolution-recrystallization process may be occurred at high temperature.

Figure 1
To investigate deeply the unexpected morphology evolution and the occurring of dissolution-recrystallization process, the as-synthesized precursor at 0 °C was hydrothermally treated at high temperature (such as for 24 h at 150 °C or 170 °C) and SEM/TEM images were shown in Figure 2. After hydrothermal treatment of sheet-like precursor at high temperature and thermal decomposition, CeO$_2$ nanopolyhedra with the size of 200-300 nm were formed as shown in Figure 2b and Figure 2c, and the polyhedral nature of the nanoparticles was confirmed once again by TEM (Figure 2d). Furthermore, the process, including the first dissolution of sheet-like precursor and then the growth into nanopolyhedra via recrystallization, was observed visually due to the existence of part sheet-like structure (Figure 2b).

Combining the above experimental results, it was reasonably believed that the lower reaction temperature was favor to the formation of sheet-like structure due to slow rate of crystalline growth and low dissolubility, however, the dissolution-recrystallization was dominant at higher temperature and finally grew into polyhedra structure.

Figure 2

Additionally, the crystal phase of as-synthesized precursors and calcined samples was investigated via XRD technique, and the corresponding XRD patterns were displayed in Figure 3. For all calcined samples (Figure 3b), all the detectable peaks in the pattern can be indexed to the pure cubic fluorite CeO$_2$ with a lattice constant $a = 0.5414$ nm (JCPDS 34-394). Using Debye-Scherrer formula, the strongest peaks (111)
at 2θ = 28.5° were used to calculate the average grain size of the CeO$_2$ particles, it was determined to be around 15-20 nm and increased with the increase of reaction temperature. No crystalline impurity was detected from the XRD spectra. However, the crystal phase of as-synthesized precursors (the uncalcined precipitates) at different temperatures was distinct. The as-synthesized samples at 0 °C and 25 °C showed an unknown phase, and the weak intensity of the pattern indicated that the samples had poor crystallinity, which was related to the low reaction temperature. When the reaction temperature was increased to 50 °C, diffraction peaks of orthorhombic cerium carbonate hydrate (Ce$_2$(CO$_3$)$_3$•6H$_2$O, JCPDS 30-295) were found in the XRD pattern and the intensity evidently increased, which indicated a good crystallinity. As the reaction temperature was further raised to 75 °C or more, the as-prepared samples showed the diffraction peaks of CeOHCO$_3$. It can be found that pure orthorhombic CeOHCO$_3$ (JCPDS 41-13) can be obtained at 75 °C and 100 °C, but hexagonal CeOHCO$_3$ (JCPDS 32-189) with a part of cubic fluorite CeO$_2$ phase (JCPDS 34-394) was formed at 150 °C. The details about phase of these precursors can be seen in Supporting Information (Figure S2). Additionally, it can be found that the crystal phase of the as-synthesized precursors transformed from the original unknown phase to CeOHCO$_3$ after the precursors prepared at 0 °C were hydrothermally treated at 150 °C and 170 °C (see Figure S2), but accompanied by a part of cubic fluorite CeO$_2$ phase. In detail, the precursors treated hydrothermally at 150 °C and 170 °C mainly exhibited the mixed crystal structure of orthorhombic and hexagonal CeOHCO$_3$ and the crystal structure of hexagonal CeOHCO$_3$, respectively, but the both accompanied
by a part of cubic fluorite CeO₂ phase. Generally, the CeOHCO₃ crystal exhibits two
important phases, i.e., orthorhombic and hexagonal phase. The orthorhombic phase is
more stable than its hexagonal phase, and the stable structure phase with lower
nucleation barrier is preferred to emerge according to the free energy and Ostwald
step rule. Thus, our results were consistent with the common idea that orthorhombic
CeOHCO₃ is the stable phase and it is difficult to get pure hexagonal CeOHCO₃ under
mild conditions. Han [20] previously reported that orthorhombic CeOHCO₃ crystals
with good crystallinity could be prepared at 160 °C, and the hexagonal phase was
formed only with the further increase of temperature and reaction period. Their results
showed that suitably higher temperature and longer time were favorable to the growth
of hexagonal CeOHCO₃ crystals.

Figure 3

More characteristics of the precursors were also investigated in its FT-IR spectra
(Figure 4). For the precursor obtained at 150 °C, the band centered at 3476 cm⁻¹ was
ascribed to the O-H stretching vibration in OH⁻ group, and the 3620 cm⁻¹ band was
normally attributed to O-H bending vibrations combined with Ce atoms. The intensive
peaks at 1510 and 1443 cm⁻¹ were assigned to the ν₃ mode of CO₃²⁻ group, and the
peaks at the 872 and 712 cm⁻¹ were assigned to the ν₂ and ν₄ modes of the CO₃²⁻
group, respectively. The peaks at 600 and 782 cm⁻¹ were also due to the vibration of
the CO₃²⁻ group. The minor peaks in 2000-3000 cm⁻¹ were assigned to C-H vibrations.
The absorption bands agreed with the ones previously reported in the literature, which
was characteristic peaks of hexagonal structure \( CeOHCO_3 \) [21]. The FT-IR spectra of
the precursors obtained at 75 and 100 °C were same, which was in good agreement
with the results of XRD showing the both were orthorhombic \( CeOHCO_3 \). Apparently,
peaks of the precursors obtained at 0, 25 and 50 °C were different with above three
samples, but these three precursors demonstrated same characteristic peaks and the
characteristic peaks of \( OH^- \) group disappeared. The strong absorption band between
1300 and 1600 cm\(^{-1}\) was due to carbonate ion stretching vibration, the sharp
absorption peaks between 600 and 900 cm\(^{-1}\) were due to carbonate ion bending
vibration, and the absorption band between 3000 and 3750 cm\(^{-1}\) was due to -OH
group of \( H_2O \). These proved that the precursor was hydrated cerium carbonate
(\( Ce_2(CO_3)_3 \cdot xH_2O \)), not the mixed salts of cerium and ammonium carbonates [22].
Additionally, according to the XRD results, the precursor obtained at 50 °C showed a
single phase of orthorhombic cerium carbonate hydrate (\( Ce_2(CO_3)_3 \cdot 6H_2O \), thus, it
was speculated that the precursors obtained at 0 and 25 °C may be a sort of cerium
carbonate hydrate with poor crystallinity.

Figure 4

Previously, a few literatures [10, 11, 23, 24] reported that sheet-like CeO\(_2\) could be
synthesized via controlling the morphology of Ce(OH)CO\(_3\) precursors, and it was
widely thought that the crystal phase of Ce(OH)CO\(_3\), hexagonal or orthorhombic
phase, was crucial. However, in our work, it was found that the petal/belt-like CeO\(_2\)
nanosheets could be obtained by the calcination of Ce\(_2(CO_3)_3\) precursors with
corresponding morphologies, while the morphology of precursors (petal or belt-like) was determined by controlling reaction temperature. For instance, limitation of the crystalline growth at low temperature (0 °C) resulted in the formation of petal-like Ce$_2$(CO$_3$)$_3$ precursor, and the higher temperature (25 °C) was favorable for the growth of crystalline along a specific direction and generated belt-like Ce$_2$(CO$_3$)$_3$ precursor.

In order to explore the effect of as-synthesized precursor, the different precipitants, such as aqueous ammonia (AA), sodium bicarbonate (SB), ammonium carbonate (AC) and sodium carbonate (SC), were investigated at 0 °C. As shown in Figure 5, sheet-like CeO$_2$ could be synthesized using SB, AC and SC as precipitants with the exception of AA (the detail SEM images can be seen in Figure S3). Among these sheet-like morphologies, the sample prepared using SB as precipitant exhibited a similar petal-like sheet with the sample obtained using ammonium bicarbonate as precipitant, while AC and SC as precipitants, plate-like CeO$_2$ could be formed and was similar with the reports of Yin [25]. Moreover, Figure 5e showed the XRD patterns of prepared precursors. The peaks of samples synthesized using AA and SC as precipitants could be indexed as the single phase of cubic fluorite CeO$_2$ and orthorhombic cerium carbonate hydrate (Ce$_2$(CO$_3$)$_3$•6H$_2$O, JCPDS 30-295), respectively. While SB and AC as precipitants, the obtained precursors were of unknown phase, but may be cerium carbonate hydrate, which was the same with that of ammonium bicarbonate as precipitant at 0 °C and 25 °C.

Figure 5
Phase of as-synthesized precursors and morphologies of CeO$_2$ at different temperatures and using different precipitants were summarized in Table 1. In our synthesis system, the possible reaction process as follows:

\[
\text{HCO}_3^-(aq) + H_2O \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^- \quad (1)
\]
\[
\text{Ce}^{3+}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{CeOH}^2+(aq) \quad (2)
\]
\[
\text{CeOH}^2+(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{CeOHCO}_3(s) \quad (3)
\]
\[
2\text{Ce}^{3+}(aq) + 3\text{CO}_3^{2-}(aq) \rightarrow \text{Ce}_2(\text{CO}_3)_3(s) \quad (4)
\]

For the formation of CeOHCO$_3$, trivalent Ce$^{3+}$ had strong affinity for OH$^-$, and formed the Ce(OH)$^{2+}$ polyatomic group. At elevated temperature, CO$_3^{2-}$ tends to bond with the positive-charged groups to yield solid CeOHCO$_3$ at high supersaturation [26]. However, our results showed that the formation of Ce$_2$(CO$_3$)$_3$ was more favorable at lower temperature, which may be associated with low concentration of OH$^-$. Thus it can be seen that, the two kinds of cerium carbonate hydrate precursors (Ce$_2$(CO$_3$)$_3$•6H$_2$O and Ce$_2$(CO$_3$)$_3$•xH$_2$O) both formed sheet-like structure at lower temperature and then transformed into CeO$_2$ via a calcination process, but the detail morphologies, such as plate-like, belt-like or petal-like, was not related with the crystal phase and the reason was still not clear. Whereas, the Ce(OH)CO$_3$ precursors obtained only at higher temperature presented irregular particle-like or polyhedral morphologies due to the dissolution-recrystallization and Ostwald ripening processes.

Table 1

Many experimental parameters such as aging time, amount of water and adding
The way of precipitant at 0 °C were investigated. The SEM images (Figure S4) showed that CeO$_2$ nanosheets could be formed even without aging, and the aging time more greatly effected the thickness of nanosheets, increasing from 30-50 nm to 70-100 nm (after aging for 48 h). Thus, except stated otherwise, the following all samples were aged for 24 h. Additionally, even amount of water decreased from 400 ml to 100 ml or 50 ml, flower-like CeO$_2$ from self-assembly of petal-like nanosheets at 0 °C still could be synthesized, and the belt-like nanosheets also could be obtained (Figure S5).

However, when ammonium bicarbonate precipitant was added into cerium nitrate solution by slowly dropping way (2.5ml/min), the obtained CeO$_2$ displayed an aggregative structure in a rod-like particles, and the precursor exhibited orthorhombic cerium carbonate hydrate (Ce$_2$(CO$_3$)$_3$•8 H$_2$O, JCPDS 38-377) phase (Figure 5f, Figure S6 and Figure S7). Therefore, it is speculated that high supersaturation was a key factor for preparing sheet-like CeO$_2$ via phase transformation of high anisotropic precursors, such as Ce$_2$(CO$_3$)$_3$, and CeOHCO$_3$.

On the basis of the experimental results, a possible growth process demonstrating the synthesis of CeO$_2$ with different morphologies can be simply described in Figure 6.

**Figure 6**

### 3.2 Characterization of petal- and belt-like CeO$_2$ nanosheets

More detailed structural information about the petal- and belt-like CeO$_2$ nanosheets was further provided by High-resolution TEM (HRTEM). Figure 7a and 7d show the
magnified image of the CeO$_2$ samples aged for 24 h at 0 °C and 25 °C, it further indicated that the both CeO$_2$ samples were sheet-like structure. Figure 7b and 7e further display that each nanosheet was composed of numerous densely packed particles, and it was the particles and their interspacing voids that were responsible for the roughness, which was similar with the reports of Deng [12]. Figure 7c and 7f directly showed that the lattice spacing was 0.30 nm, close to the (111) lattice spacing of the cubic phase of CeO$_2$. This result indicated that the exposed facets of the both nanosheets are (111) facets. Additionally, the corresponding selected area electron diffraction (SAED) pattern (Figure 7c and 7f) indicated that the CeO$_2$ nanosheets both are polycrystal structure with some defects.

Figure 7

Figure 8 showed the H$_2$-TPR and CO$_2$-TPD results of the two types of CeO$_2$ nanosheets, compared with the CeO$_2$ nanoparticles prepared by thermal decomposition method (CeO$_2$-TD). The petal-like (CeO$_2$-0) and belt-like CeO$_2$ (CeO$_2$-25) nanosheets both exhibited a broad peak between 300 and 550 °C centered at 500 °C that was attributed to less reactive surface oxygen species, and the hydrogen consumption of CeO$_2$-25 sample was slightly higher than that of CeO$_2$-0. The reduction above 750 °C was related to the reduction of lattice oxygen. For the CeO$_2$-TD sample, there are two overlapping peaks centered at 420 and 520 °C, respectively. By contrast, the reduction properties (such as oxygen mobility and oxygen storage capacity) of CeO$_2$ nanosheets are not superior to the CeO$_2$-TD sample.
As shown in Figure 8b, three samples displayed two peaks of CO$_2$ desorption at low temperature range, one at 150-170 °C, corresponding to the weak basic sites, another with the maximum at about 330 °C, associated with medium-strength basicity. Additionally, the amount of base sites of CeO$_2$-25 was obvious greater than that of CeO$_2$-0 and CeO$_2$-TD samples, which probably came from the larger surface areas and more number of defects in the framework of the CeO$_2$-25 sample, i.e. the number of oxygen atoms associated with Ce exhibiting a low coordination number.

Figure 8

3.3 Catalytic oxidation of CO

The catalytic CO oxidation performances of synthesized CeO$_2$ nanosheets and CeO$_2$ nanoparticles prepared by thermal decomposition method were shown in Figure 9. CeO$_2$ nanosheets (petal-like CeO$_2$-0 and belt-like CeO$_2$-25) exhibited higher conversion than CeO$_2$ nanoparticles prepared by thermal decomposition method, but CeO$_2$-25 sample was slightly better, especially at higher temperature. However, the catalytic activity was not directly related to the reduction properties of CeO$_2$ displayed in Figure 9a, which showed the CeO$_2$-TD could be reduced at lower temperature. Therefore, it can be considered that the enhanced catalytic activity could be attributed to their higher specific surface area, and the BET surface area of CeO$_2$-25 and CeO$_2$-0 was 68 cm$^2$/g and 15 cm$^2$/g, but the CeO$_2$-TD (45 cm$^2$/g) did not show a better activity than CeO$_2$-0. Additionally, compared with CeO$_2$ nanoparticles, the CO$_2$ adsorbed on surface of the CeO$_2$ nanosheets from the complete oxidation of CO more easily desorbed (seen in Figure 8b) and the more base sites presented on CeO$_2$.
nanosheets, which could be another more important reason.

Figure 9

3.4 Catalytic oxidation of 1, 2-dichloroethane

The light-off curves and stability tests at 250 °C of 1, 2-dichloroethane (DCE) catalytic oxidation recorded at constant GHSV (15,000 h⁻¹) and feed concentration (550 ppm in air) over different CeO₂ and vanadia supported CeO₂ catalysts were presented in Figure 10. Three pure CeO₂ catalysts revealed almost overlapping activity curves except that at 250 °C, and the conversions of DCE at 250 °C were 90%, 80% and 70% over CeO₂-25, CeO₂-0 and CeO₂-TD catalysts, respectively. Moreover, the stability tests at 250 °C showed the conversion over all pure CeO₂ catalysts sharply dropped to 20-40% within 300 min, by contrast, the decline of CeO₂-TD catalyst was more severe and the conversion fell to about 20% only after 150 min. Compared with pure CeO₂ catalysts, the catalytic activities of the CeO₂ catalysts supported 5%wt vanadia were improved obviously, especially 5%wt VOₓ/CeO₂-25 and 5%wt VOₓ/CeO₂-0, for example, the T₅₀% of 5%wt VOₓ/CeO₂-25 decreased from 210 °C to 175 °C and T₉₀% reduced from 250 °C to 225 °C. Moreover, the two kind of nanosheets supported catalysts also exhibited an almost same activity, being consistent with the results of pure CeO₂ catalysts, but a remarkable higher conversion than nanoparticles catalyst. The difference of catalytic activities between vanadia supported on CeO₂ nanosheets and nanoparticles may be from the high dispersion of vanadia on CeO₂ nanosheet due to its large surface areas and the easier dispersion
over sheet-like CeO$_2$ than that particle-like CeO$_2$, which was favor to the expose of
surface active sites of CeO$_2$, because CeO$_2$ is considered as the main active
components for the catalytic combustion of chlorinated organic compounds over
CeO$_2$ based catalysts [27]. Additionally, the stability tests at 250 °C showed that the
CeO$_2$ nanosheets supported vanadia both presented a better stability, the conversion of
tetra halo ethylene (DCE) decreased from 97% to 92% in the last 40 min and then maintained stable for at
least 400 min. Similar with the pure CeO$_2$ catalysts, the decline of VO$_x$/CeO$_2$-TD
catalyst was greater, from 86% to 62%. Thus it can be seen, the loading of vanadia
apparently improved the stability of CeO$_2$ (whether sheet-like CeO$_2$ or traditional
CeO$_2$ particle) for catalytic oxidation of DCE.

More importantly, large amounts of vinyl chloride (VC) could be detected over all
pure CeO$_2$ catalysts, while only trace of VC was observed over vanadia supported
catalysts. Vinyl chloride, usually as intermediate was found during the catalytic
oxidation of DCE over HZSM-5 solid acid catalysts, being stable, does not undergo
further dehydrochlorination and oxidized to CO, CO$_2$ and HCl even at 400 °C [28],
due to the absence of oxidative active sites over the solid acid catalysts. Thus, the
presence of VC suggested that the abstraction of HCl (dehydrochlorination) also was
the first step for the catalytic oxidation of DCE over the CeO$_2$ based catalysts.

Furthermore, CeO$_2$ supported vanadia catalysts possessed more excellent oxidation
performance compared with pure CeO$_2$, the H$_2$-TPR profiles of VO$_x$/CeO$_2$ catalysts
was listed in Figure 11, which contributed to the complete oxidation of VC
intermediate into CO$_2$ and HCl.
4. CONCLUSIONS

In summary, petal-like and belt-like CeO$_2$ nanosheets have been synthesized by an aqueous phase precipitation method and NH$_4$HCO$_3$ as precipitant. In this procedure, any organic solvent and template or surfactant was not required, moreover, the preparing conditions were very mild and reaction temperature varied from 0 °C to 25 °C without hydrothermal or solvothermal treatment. The reaction temperature and supersaturation played key roles in the formation of ceria nanosheets, namely, lower temperature and higher supersaturation were favorable to the synthesis of sheet-like cerium carbonate hydrate by oriented aggregation process, whereas the elevated temperature could cause the dissolution-recrystallization and Ostwald ripening of precursors and then formed polyhedral CeO$_2$ by a thermal decomposition process. Additionally, compared with traditional CeO$_2$ nanoparticles, the pure ceria nanosheets and supported vanadia showed more excellent catalytic oxidation activities for catalytic oxidation of CO and 1, 2-dichloroethane. Especially, the VO$_x$/CeO$_2$ nanosheets showed a very promising application in the catalytic combustion of chlorinated volatile organic compounds (CVOCs). The findings of this work not only provided a simple means to achieve control of the morphology (from sheet-like to polyhedron) but also demonstrated that the catalytic oxidation performances can be enhanced by the variation of CeO$_2$ morphology.
ACKNOWLEDGMENTS

This research was supported by National Natural Science Foundation of China (Nos.21307033, 21277047), National Basic Research Program of China (Nos. 2010CB732300, 2011AA03A406), Shanghai Natural Science Foundation (No. 13ZR1411000), Commission of Science and Technology of Shanghai Municipality (No. 11JC1402900), Development Program for Young Teachers in Shanghai Universities and the Opening Project of Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Chinese Academy of Sciences (NRNE-OP2012001).

REFERENCES


Table/ Figure Captions

Table 1 Phase of as-synthesized precursors and morphologies of CeO$_2$ at different temperatures and using different precipitants

Figure 1. SEM images of synthesized CeO$_2$ at different temperature (aging for 15 h): (a) 0 °C, (b) 25 °C, (c) 50 °C, (d) 75 °C, (e) 100 °C and (f) 150 °C.

Figure 2. SEM and TEM images of synthesized CeO$_2$: (a) as-synthesized precursor at 0 °C, (b) hydrothermally treated (a) sample at 150 °C, (c) hydrothermally treated (a) sample at 170 °C, (d) TEM of (c) sample.

Figure 3. XRD patterns of as-synthesized precursors (a) at different temperature and calcined samples (b).

Figure 4. FT-IR spectra of as-synthesized precursors at different temperature.

Figure 5. SEM images of samples prepared using different precipitants and XRD patterns of as-synthesized precursors: (a) aqueous ammonia (CeO$_2$-AA), (b) sodium bicarbonate (CeO$_2$-SB), (c) ammonium carbonate (CeO$_2$-AC), (d) sodium carbonate (CeO$_2$-SC), (e) XRD of a, b, c and d as-synthesized precursors, (f) ammonium bicarbonate as precipitant by slowly dropping way.

Figure 6. Schematic description of the growth process of CeO$_2$ with different morphologies.

Figure 7. HRTEM images of synthesized CeO$_2$ nanosheets prepared at 0 °C (a-c) and 25 °C (d-f).

Figure 8. H$_2$-TPR (a) and CO$_2$-TPD (b) profiles of CeO$_2$ nanosheets synthesized at 0 °C and 25 °C, and CeO$_2$ particles prepared by thermal decomposition method.
Figure 9. The catalytic performance of CeO$_2$ nanosheets for CO oxidation.

Figure 10. Light-off curves and stability tests of 1, 2-dichloroethane catalytic oxidation over CeO$_2$ and vanadia supported CeO$_2$ catalysts.

Figure 11. H$_2$-TPR profiles of vanadia supported CeO$_2$ nanosheets and CeO$_2$ particles.
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