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Morphology-dependent properties and adsorption performance of CeO_2 for fluoride removal

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ABSTRACT

Three kinds of CeO_2 materials with different morphologies (nanorods, octahedron and nanocube) were prepared by simple hydrothermal method. Adsorption behaviors of fluoride onto the three CeO_2 materials were investigated. Three CeO_2 materials exhibited different adsorption performance for fluoride. The CeO_2 nanorods mainly exposed {1 0 0} and {1 1 0} planes had the highest adsorption capacity for fluoride, whereas the CeO_2 nanocubes with {1 0 0} planes exposed showed the lowest adsorption capacity. Characterization results showed that the three CeO_2 materials with different morphologies showed different physical and chemical properties, which may result in big difference in their removal mechanism for fluoride, and thus displayed different adsorption performances for fluoride removal. The removal mechanism of fluoride on the three CeO_2 mainly included Ce^{3+}-O defect, ion exchange, surface adsorption and pore filling.

1. Introduction

Recently, CeO_2 attracted more and more attention in heterogeneous catalysis due to its high oxygen storage and release capacity, facile oxygen vacancy formation ability, and unique electronic properties related to its highly localized 4f orbitals [1,2]. Compared with bulk CeO_2, nanoscaled CeO_2 can offer relatively larger specific surface area and more active sites [3], thus resulting in the excellent performance.

In fact, the morphology of CeO2 also has a decisive influence on its performance besides the effect of nanoscale. Many studies have shown that CeO_2 properties are closely related to its morphology [4–7], and the exploration of the morphology-performance relation still is widely investigated by researchers [8–11]. Tan et al. [4] found that the support morphology of CeO_2 has a significant effect on the catalytic activity of Pd/CeO_2 catalyst for formaldehyde oxidation. The palladium nanoparticles loaded on CeO_2 nanocubes exhibited much higher activity than nanooctahedrons and nanorods. Mai et al. [10] reported that CeO_2 nanorods and nanocubes were more active for CO oxidation than CeO_2 nanoparticles. One of the reasons is that the CeO_2 materials with different morphology exposed different crystal faces, will display distinct reactivity. For instance, the CeO_2 nanorods with {1 1 0} face exposed are easier to produce oxygen vacancy, and thus exhibit a higher CO catalytic oxidation activity than conventional nanoparticles [12,13]. Therefore, it is possible to achieve an adjustable reaction activity by establishing a relationship between morphology and performance of the CeO_2. However, researches on the morphology effects of CeO_2 are mainly focused on the heterogeneous catalysis, while the exploration is less in water treatment. Especially, seldom attention is devoted to the relationship between morphology and removal performance for fluoride by CeO_2. Therefore, it is of interest to tune the distinct defluorination behavior of the CeO_2 materials with different morphologies.

However, three issues are unclear with respect to the effects of CeO_2 morphology on the fluoride removal presently. ① Whether CeO_2 morphology will affect its adsorption performance for fluoride? ② What is the effect of morphology on the adsorption properties of the material for fluoride? ③ How the morphology affects its adsorption performance for fluoride? Based on study of the effect of material morphology on its physic-chemical property and defluoridation performance, our ultimate goal is to establish the relationship among material morphology, physic-chemical property and adsorption performance, thus providing new thought and approach for the development of high efficiency defluoridation material.

In this work, three different morphologies of CeO_2 (nanocubes,

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octahedrons, and nanorods) were prepared, which exhibited different removal performance for fluoride. The CeO_2 nanorods showed the best removal ability for fluoride, as compared with the CeO_2 nanocubes and CeO_2 octahedrons. The morphological influence on the removal performance of fluoride was established, and the adsorption mechanism of fluoride on CeO_2 was proposed.

2. Experimental section

2.1. Preparation of CeO_2

All of the reagents, including cerium nitrate ($Ce(NO_3)_3·6H_2O$) and sodium hydroxide (NaOH), were analytically pure and purchased from Sinopharm Chemical Regent Beijing Co., Ltd. They were used without further purification throughout synthesis processes. The synthesis of CeO_2 nanorods, octahedrons and nanocubes was based on the reported methods [4]. The CeO_2 nanocrystals exposing different facets were hydrothermally synthesized with $Ce(NO_3)_3·6H_2O$ as precursor. The preparation of CeO_2 with different morphologies followed the same procedure except different dosages of $Ce(NO)_3·6H_2O$ and NaOH and reaction temperatures used. For the CeO_2 nanorods, 3.6 g of $Ce(NO_3)_3·6H_2O$ was dissolved in 10 mL of ultrapure water, and then 70 mL of 6 M NaOH solution was added by dropwise into the solution under vigorous magnetic stirring for several minutes. The as-obtained slurry was transferred into a Teflon-lined stainless steel autoclave and hydrothermally heated at 100 °C for 24 h. After cooling naturally, the precipitate was collected by centrifugation, thoroughly washed with ultrapure water and ethanol several times to remove impurities, and followed by drying in oven at 60 °C overnight. To obtain the CeO_2 nanocubes, 1.0 g of $Ce(NO_3)_3·6H_2O$ and 8.0 g of NaOH was used, and the reaction temperature was set to 200 °C for 24 h. To prepare the CeO_2 octahedrons, the amount of $Ce(NO_3)_3·6H_2O$ and NaOH was 3.9 g and 0.16 g, respectively, and then hydrothermal treatment at 180 °C for 12 h. For simplicity, the as-obtained CeO_2 nanorods, octahedrons and nanocubes were denoted as CeO_2-Rods, CeO_2-Octs and CeO_2-Cubes, respectively.

2.2. Characterization of the CeO_2

High-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) was used to observe size and morphology of the as-obtained CeO_2 materials, operating at an acceleration voltage of 200 kV. The composition of the prepared CeO_2 samples were characterized by powder X-ray diffractometer (XRD, Rigaku D/max 2500), with Cu Kα radiation ($\lambda = 1.5406$ Å), employing a scanning rate $0.02\ °s^{-1}$ in the 2θ ranging from 5 to 80°. Element composition and valence state of the three CeO_2 products were analyzed using the X-ray photoelectron spectroscopy (XPS, ESCALab220i-XL). The binding energies were referenced to the adventitious C 1s line at 284.8 eV. Raman spectra of the samples were collected under ambient conditions on a LabRAM Aramis Raman Spectrometer (HORIBA Jobin Yvon S. A. S.) equipped with an excitation laser of 532 nm. The surface functional groups of the three CeO_2 were measured by the Fourier transform infrared spectroscopy (FTIR, Tensor 27). The surface area and pore size distribution of the as-obtained CeO_2 were obtained using an automated gas sorption analyzer (Quantachrome Instruments, autosorb-iQ).

2.3. Adsorption experiments

Fluoride stock solution was prepared with ultrapure water using NaF. Batch adsorption experiments were conducted to obtain the adsorption isotherm of fluoride. All adsorption experiments were carried out in 50 mL polypropylene cap-contained flasks containing 40 mL of fluoride solution and 20 mg of adsorbent. These flasks were placed in a temperature controlled (at 25 ± 1 °C) shaker for a predetermined contact time at 200 rpm. Kinetic studies were performed by batch experiment under a fixed initial fluoride concentration of 50 mg/L. It contained a series of flasks, and one of them was used to measure the residual fluoride concentration at a predetermined time. Adsorption isotherms were conducted with fluoride initial concentrations ranging from 5 to 150 mg/L. The effect of pH on the fluoride adsorption was conducted by adjusting the initial solution pH to a predetermined value in the range of 2–11 using HCl (0.1 mol/L) and NaOH (0.1 mol/L) solution with an initial fluoride concentration of 50 mg/L. The solution was then filtered with 0.22 μm membrane filter for analysis. Herein, ion chromatography (ICS-900, Dionex) was used to analyze the residual fluoride concentration. The adsorption capacity q_e (mg/g) was calculated by the following equation:

$$q_e = \frac{(C_0-C_e)V}{m} \tag{1}$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of fluoride, respectively; V (L) is the solution volume and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characterization of CeO_2 materials

Microstructure and morphology of the three CeO_2 samples were observed by HRTEM, as shown in Fig. 1. The CeO_2-Rods display well-defined rod-like structure with an average diameter of about 15–25 nm and length of about 200 nm (Fig. 1a). The HRTEM image (Fig. 1b) shows that the interplanar spacings are 0.27 and 0.19 nm, which can be ascribed to (2 0 0) and (2 2 0) facet of CeO_2, respectively [14]. It indicates that the as-obtained CeO_2 nanorods have preferential growth along the [1 1 0] direction and mainly expose the {1 0 0} and {1 1 0} planes. As shown in Fig. 1c, the CeO_2-Octs consist of well-defined hexagonal structure with an average size approximately 14 nm. An interplanar spacing of 0.31 nm can be observed in the HRTEM image (Fig. 1d), which corresponds to {1 1 1} planes of the CeO_2 octahedrons. Fig. 1e presents low-resolution HRTEM image of the square-shaped CeO_2 nanocubes with the average sizes approximately 25 nm. The HRTEM image in Fig. 1f displays that the lattice fringe assigned to the (2 0 0) facet with an interplanar spacing of 0.27 nm, belonging to the {1 0 0} plane. In conclusion, the as-obtained CeO_2 nanorods, octahedrons and nanocubes provide crystallographically dominant planes of {1 1 0}, {1 1 1} and {1 0 0}, respectively, which may have different chemical properties, and hence show distinct removal performance for fluoride.

Fig. 2 shows the XRD patterns of the three CeO_2 materials. The characteristic diffraction peaks, observed at 2θ = 28.6, 33.1, 47.5, 56.3, 59.1, 69.4, 76.7 and 79.1°, correspond to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) plane diffraction patterns of the face-centered cubic (fcc) fluorite structure of CeO_2 (JCPDS No. 34-0394). No impurity peaks are observed, confirming the high crystalline purity of the as-obtained CeO_2 materials. It is worth noting that the three CeO_2 materials display distinct intensity and full width at half maximum (FWHM) of the diffraction peaks, indicating they have different crystallinity and crystallite size. Generally, sharp and intense diffraction peaks are indicative of high crystallinity of the obtained material. The broadening diffraction peaks of the CeO_2 nanorods distinctly reflect its poorly crystalline nature, which can be seen clearly from its crystallinity value, as summarized in Table 1. The values of crystallinity are 61.6, 67.3 and 96.4% for the CeO_2 nanorods, octahedrons and nanocubes, respectively. The grain sizes of the CeO_2-Rods, CeO_2-Octs and CeO_2-Cubes are calculated to be 12.8, 12.9 and 24.6 nm, respectively, according to the Scherrer equation and the prominent (1 1 1) diffraction peak (Table 1). In addition, the lattice parameters of three CeO_2 materials are in the following order: CeO_2-Rods > CeO_2-Octs > CeO_2-Cubes.

Based on the above analysis, the CeO_2-Rods have the lowest