Honeycomb nano cerium oxide fabricated by vacuum drying process with sodium alginate

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Abstract. Nano cerium oxide (CeO2) with honeycomb structure were synthesized simply and rapidly by vacuum drying method with sodium alginate as the biological template agent, Ce(NO3)3·6H2O as cerium source. The composition, aperture size, specific surface area and morphology of the prepared samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), N2 adsorption-desorption and scanning electron microscopy (SEM). Simultaneously, the effects on the morphology of the samples, which were caused by the drying method and the concentration of sodium alginate, were investigated. The results indicate that the prepared samples were nano CeO2 with high crystallinity and uniform dispersion, most of which had mesoporous, macroporous and honeycomb structure. The specific surface area of CeO2 is 210.0 m2/g, and the average aperture is 12.77 nm. The prepared samples can act as catalyst in the catalytic wet oxidation process for the treatment of high concentration organic wastewater, and the COD removal rate could exceed 90%.

1. Introduction

Cerium oxide (CeO2), as a typical rare earth oxide, is widely used as a promoter in three-way catalysts (TWCs) for the elimination of toxic auto-exhaust gases, oxygen permeation membrane systems, ultraviolet absorption, as well as environmental chemistry, etc.[1-5] The different application properties of nano CeO2 are directly related to its structure and morphology. So the study on the structure and morphology of nano CeO2 attracts so much attention.[6-8] At present, the structure according to the different dimensions of the nano CeO2 can be divided into one-dimensional nano tube, nano wire and nano rod, two-dimensional nano sheet, nano disk and three-dimensional nano ball.[9, 10] The various structures of nano CeO2 are fabricated by coprecipitation, sol-gel method, hydrothermal synthesis and template method.[11-14] And biological template method for metal oxide preparation is a kind of environment-friendly and low cost method. Among biological templates that have been developed, sodium alginate is a polysaccharide, and extracted from brown algae. Alginites belong to exopolysaccharides and are non-repeating copolymers composed of β-D-mannuronic acid (M) and α-L-guluronic acid (G) which are linked by 1-4 glycosidic bonds. Since its safety and biocompatibility, abundant reserves and renewable, it is...
widely used in the field of membrane science, food industry, biological medicine, pollution control, etc.[15]

In this work, honeycomb nano CeO2 was fabricated by vacuum drying process with sodium alginate as template. The work focused on the influence of process parameters on the microstructure of the material. Meanwhile, the catalytic performance was examined by catalytic wet oxidation treatment with high concentration organic wastewater.

2. Experimental

2.1. Preparation of materials
All chemical reagents were of analytical grade and used without any further purification. In a typical synthesis, Ce(NO3)2·6H2O was dissolved in deionized water to produce a transparent solution of 10 mol/L. Then added 2 mL Ce(NO3)2·6H2O solution prepared into 10 mL 1% sodium alginate solution. After being stirred at room temperature, the mixture turned into a homogeneous gel, and then the gel was dried in vacuum -0.06 MPa at 30 °C for 5 h. Then the yellowish ceria powder with nanostructures was obtained by calcining at 600 °C for 2 h.

2.2. Characterization
The prepared samples were characterized by several instrumental analysis techniques. The crystallinity of the samples was measured with powder X-ray powder diffraction patterns which were obtained on a Bruker diffractometer using CuKα radiation (λ=0.1547 nm). BET measurements including surface areas and pore volumes were performed using an automatic physical static analyzer (Quantachrome, Autosorb-IQ2-MP). The samples were degassed at 300 °C for 3 h and characterized at liquid nitrogen temperature (77.350 K). SEM images were collected with a Hitachi SU8010 microscope. The FTIR spectra were recorded at room temperature using Agilent Technologies FTIR-660+610 spectrometer over the range of 400-4000 cm⁻¹.

2.3. Measurement of catalytic activity
The prepared samples were used as catalyst in the experiment of catalytic wet oxidation treatment of high concentration organic wastewater. Added 0.2 g prepared samples and 1 mL H2O2 (6%) into 50 mL wastewater taken from acrylic chemical factory. The mixture was stirred at room temperature for 3 h, and then placed into microwave reactor at 100 °C for 40 min. After reaction, the COD value of wastewater was determined.

3. Results and discussion

3.1. Characterization analysis by XRD
Fig. 1 shows the XRD patterns of the as-made nanostructure. The results match with PDF#34-0394-CeO2 comparisons. Clear crystal lattice diffraction peaks appear at 28.5°, 33.1°, 47.6°, 56.5°, 59.3°, 69.7°, 77.1°, 79.5° and 89.0°, which indicate that the prepared sample CeO2 has high crystallinity and uniform dispersion.
3.2. Characterization analysis by FTIR

Fig. 2 shows the comparisons between sodium alginate and the sample with FTIR spectra. In contrast with A, the absorption peak of B at 3446 cm\(^{-1}\) is the O-H bond of sodium alginate chains which shifts to low wave number direction. That is because the oxygen atom of the carbonyl group on the macromolecular chain forms an association with Ce\(^{2+}\), which produces chelate effect, and also the bending vibration absorption of O-H decreases. The absorption peak of B at 1417 cm\(^{-1}\) is decreased, which belongs to C-H bond in-plane bending vibration absorption peak. That is because the association of alginate molecular chain and the formation of network structure limit the vibration of the C-H bond, and then the absorption peak decreases. The absorption peak of B at 1350 cm\(^{-1}\) is enhanced which is the C=O bond stretching vibration peak. The reason lies in the role of carboxyl and Ce\(^{2+}\). In summary, the oxygen atoms of O-H bond and C=O bond in alginate molecular chains produces the chelate effect with Ce\(^{2+}\). And the formed "egg box" structure promotes the internal network structure formation of alginate.

3.3. Characterization analysis by N2 adsorption-desorption

Fig. 3 shows the N2 adsorption-desorption isotherm of CeO2. The pore characteristics of the samples can be determined by adsorption and desorption isotherms.
According to the BET classification of the adsorption isotherms, the adsorption isotherm of CeO2 is found to be close to that of the Type II adsorption isotherm (presents reverse "S" shape) [21]; the front adsorption curve rises slowly, slightly upward convex; the back end rises dramatically; even the relative pressure is close to 1.0, there is no significant adsorption saturation phenomenon presents. It is shown that there appears capillary condensation phenomenon in the N2 adsorption process, and the sample contains a certain amount of mesopores and macropores.

The adsorption and desorption isotherms of the sample adsorption isotherms do not coincide in the part of high pressure, but form adsorption loop. The type of loop reflects the characteristics and types of pore structure. Four different types of adsorption loops are recommended by International Union of Pure and Applied Chemistry (IUPAC).[22] The adsorption curve of the sample is very steep near the saturated vapor pressure, while the desorption curve is steep at medium pressure. This is close to type H3 loop recommended by the IUPAC. It indicates that the pores of prepared samples are mainly composed of nanopores, and the pore morphology is open mainly open hole such as cylinder hole with both ends opens, parallel plate hole with four sides open, and so on. The opening degree of pore is related to the rising rate of adsorption curve, the greater the pore opening, the faster the curve rise.

Calculating aperture by BJH model, the most probable aperture of CeO2 is 5.3 nm. The specific surface area and average aperture of the CeO2 obtained by BET method is 210.0 m2/g and 12.77 nm, respectively.

3.4. Characterization analysis by SEM

3.4.1. Morphology of samples at different magnification. The morphology of samples was observed using magnification of 5 K and 20 K, and the results are shown in Fig. 4. The honeycomb structure can be observed clearly in figure, which is consistent with the result of N2 adsorption-desorption isotherms.
3.4.2. The influence of drying methods on morphology. The samples were prepared in two ways: ordinary hot air drying (40 °C, 48 h dehydration) and vacuum drying (-0.06MPa, 30 °C, 5 h dehydration). The SEM scanning results of prepared samples are shown in Fig. 5. Ordinary hot air dried samples (Fig. 5 (A)) shows appearance of pore shrinkage and compact structure. This is because the material would lose water, shrink, and adhere together during ordinary hot air drying, and the more water loss, the stronger the adhesion. While the internal structure of vacuum dried samples (Fig. 5 (B)) is loose. This is because the dehydration process of material was performed in a vacuum state, the difference between internal and external pressure leads to the loose structure and easier to form honeycomb structure.

3.4.3. The influence of sodium alginate concentration on morphology. The effect of sodium alginate concentration on the morphology of the prepared samples was investigated at a concentration of 0.5%, 1.0% and 0.5 %, and the results are shown in Fig. 6, respectively. Sodium alginate solution has the characteristics of non-newtonian fluid, its viscosity increases with the increase of solution concentration. When sodium alginate concentration is low (0.5%), it is difficult to form three-dimensional structure; with the increase of the sodium alginate concentration (1%), the molar number of sodium alginate in unit volume increases, at the same time hydrogen-bonding is enhanced so that porous material presents honeycomb three-dimensional structures; when the sodium alginate dosage continued to increase (2%), the solution viscosity increases, and because of the slow migration of water and sodium alginate molecules, the resulting crystal structure has no obvious structural features.
The concentration of sodium alginate is directly related to the viscosity of the solution, and then affects the microstructure of the samples prepared.

![SEM images of the samples prepared at different sodium alginate concentration (A: 0.5%, B: 1.0%, C: 2.0%)](image)

**Fig.6** SEM images of the samples prepared at different sodium alginate concentration (A: 0.5%, B: 1.0%, C: 2.0%)

3.5. **Catalytic performance test**

1mL 6% H2O2 and 0.2 g prepared nano CeO2 were added into 50 mL acrylic chemical wastewater, and then mixed with a magnetic stirrer for 1 h in a constant temperature. Subsequently, the mixture was reacted in the microwave reactor at 100 °C for 40 min. The test results prove that the removal rate of COD was above 90%.

4. **Conclusion**

(1) It is feasible to prepare porous nano CeO2 with honeycomb structure using sodium alginate as template and under vacuum drying conditions. This method has the advantages of simple operation, mild condition, energy saving and consumption reducing. Meanwhile, compared with other templates, sodium alginate exhibits the benefits of biological materials: wide source, low price, environment friendly and so on.

(2) The drying method and the concentration of sodium alginate can affect the morphology of the samples. Vacuum drying is easier to form honeycomb structure than ordinary hot air drying, and its drying time is much shorter than the ordinary hot air drying. Too high or too low concentration of sodium alginate is not conducive to the formation of honeycomb structure. The porous nano CeO2 with honeycomb structure is obtained at the sodium alginate concentration of 1.0%.

(3) The prepared samples were applied to the treatment of high concentration organic wastewater by catalytic wet oxidation. The removal rate of COD gained from test was above 90%, which indicates that the prepared porous nano CeO2 has good catalytic performance.
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