

## Synthesis CeO<sub>2</sub> on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support by Spray Pyrolysis

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**ABSTRACT:** In the process of spray pyrolysis, the pyrolysis temperature, particle residence time in the hot zone and so on impact of the product crystal form. Spray pyrolysis is used to synthesize CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. The pyrolysis temperature is at a range of 900~1100°C, with a particle residence time in the hot zone for 2.6~3.0 second, the CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was obtained. The analysis of measuring Cl concent, and characterized by X-ray diffraction (XRD), scanning electron microscopy SEM-EDS plane scan analysis, and laser particle size analysis.

### Introduction

Automotive catalysts have been widely used to reduce emissions of hydrocarbon, carbon monoxide and nitrogen oxides from gasoline engine powered vehicles<sup>[1]</sup>. As one of the most reactive rare earth materials, ceria (cerium oxide, CeO<sub>2</sub>) has attracted a great deal of attention due to its unique applications in conversion catalysts, three-way catalysts (TWCs)<sup>[2]</sup>. CeO<sub>2</sub> is a crucial component of emission control catalysts, mainly on account of its role in oxygen storage<sup>[3]</sup>. The facile Ce<sup>4+</sup>/Ce<sup>3+</sup> redox reaction is believed to be the driving force leading to this behavior. The oxygen produced via the redox process  $2\text{CeO}_2 \leftrightarrow \text{Ce}_2\text{O}_3 + 1/2\text{O}_2$  can be utilized under reduction conditions<sup>[4]</sup>.

Supported active ingredient on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have been used widely and efficiently for the oxidation of VOCs<sup>[5]</sup>.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are intermediate phases formed in the process of thermally transforming aluminum hydroxides and oxyhydroxides into thermodynamically stable corundum or R-alumina. These high surface area aluminas have enormous commercial importance as adsorbents and catalyst components in many chemical processes, including the three-way catalysts<sup>[6]</sup>.

Spray pyrolysis by decomposition of single inorganic precursors in the air, which is a “green” method. At the same time, hydrogen chloride produced by the exhaust gas is absorbed directly, so the whole process has the advantage of short residence time, high production efficiency, low operating cost and energy consumption. During the preparation process, atomized droplets of a precursor solution undergo evaporation and shrinkage while flowing through a high-temperature reactor and eventually form particles. Due to the fact of evaporation, precipitation, drying and decomposition occurring in a dispersed phase and a single step, it becomes possible to control the key particle properties (size, morphology, chemical composition, etc.) easily by controlling the process parameters (residence time and decomposition temperature)<sup>[7-11]</sup>.

In this work, synthesize CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support using spray pyrolysis by controlling the pyrolysis temperature and particle residence time in hot zone. The analysis of measuring Cl concent, and characterized by X-ray diffraction (XRD), scanning electron microscopy SEM-EDS plane scan analysis.

## MATERIAL AND METHODS

### CeO<sub>2</sub> on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support synthesis

Solutions of AlCl<sub>3</sub>·6H<sub>2</sub>O (AR, >99.0%, Sinopharm Chemical Reagent Co. Ltd.) were used as the precursors. The Ce-containing solution was added to the Al-containing solution in a molar ratio of 1:6. The concentration of the precursors was 20.0 wt%. The schematic representation of the spray pyrolysis equipment shown in Fig.1. the spray pyrolysis system consisted of a home-made atomizer, a corundum tube located inside a tubular furnace, three cyclones as the collectors, a gas buffer tank and a tail gas absorber. Precursor droplets were sprayed by expanding compressed air through the atomizer full of atomization. After passed through the diffusion dryer, these partly dried droplets were carried into the corundum tube housed inside the tubular furnace, and the resultant pyrolysate was finally collected by a filter sampler. The roasting temperature was controlled and adjusted in the range of 900~1100°C, with a residence time of 2.6~3.0 seconds.

### Characterization of Prepared Particles.

The crystalline structure of the products was determined by a powder X-ray diffraction (XRD) (X' Pert Pro, PANalytical Corporation, Netherland) with Cu K  $\alpha$  radiation ( $\lambda = 0.154\text{nm}$ ) at 40 kV and 40 mA. The scan rate was  $4^\circ 2\theta \cdot \text{min}^{-1}$ , and the scan range is from  $10^\circ$  to  $90^\circ 2\theta$ . Peak positions and relative intensities were characterized by comparison with International Centre for Diffraction Data (ICDD) files. IR spectra were measured with a Perkin Elmer Spectrum GX FT-IR spectrometer. The TEM examinations were performed using a TEM instrument (Tecnai G220; FEI, USA) operating at 200 kV. Al<sub>2</sub>O<sub>3</sub> samples were collected directly onto Cu microgrids, and a droplet of suspending liquid was deposited onto a Cu microgrid and allowed to dry. SEM images were obtained on a Zeiss ULTRA plus SEM equipped with energy dispersive X-ray spectroscopy (EDS), which was utilized to observe the SEM microstructure.

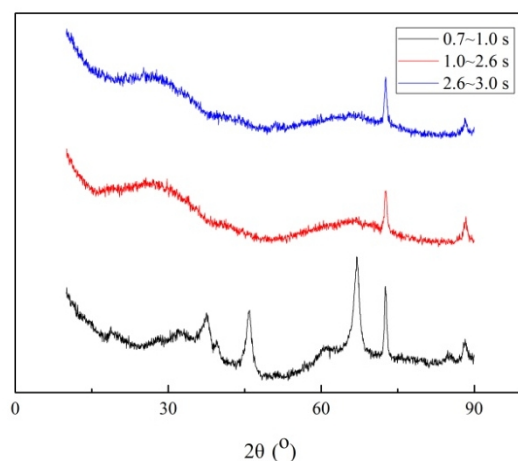


Fig. 1. X-ray diffraction patterns of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different residence time in the hot zone.

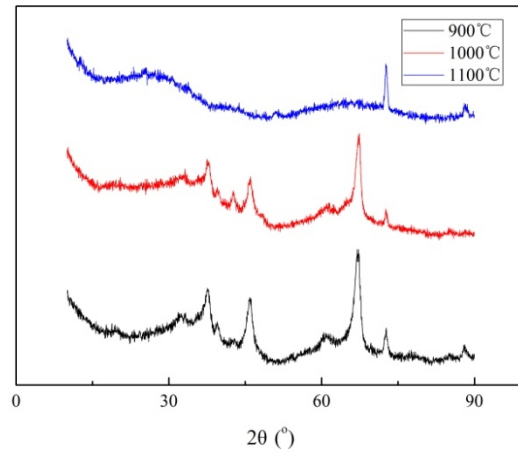


Fig. 2. X-ray diffraction patterns of  $\gamma$ - $\text{Al}_2\text{O}_3$  at different pyrolysis temperatures.

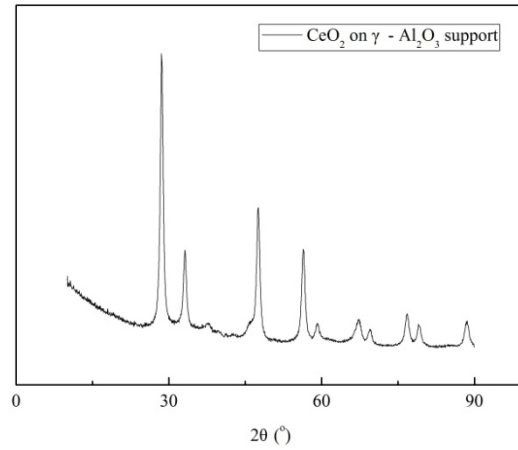
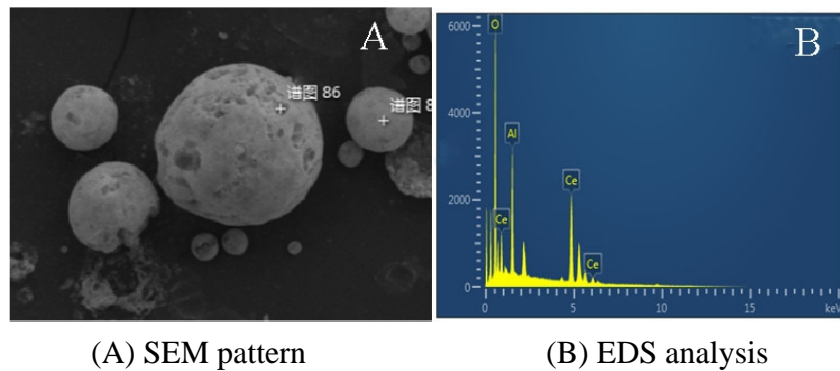
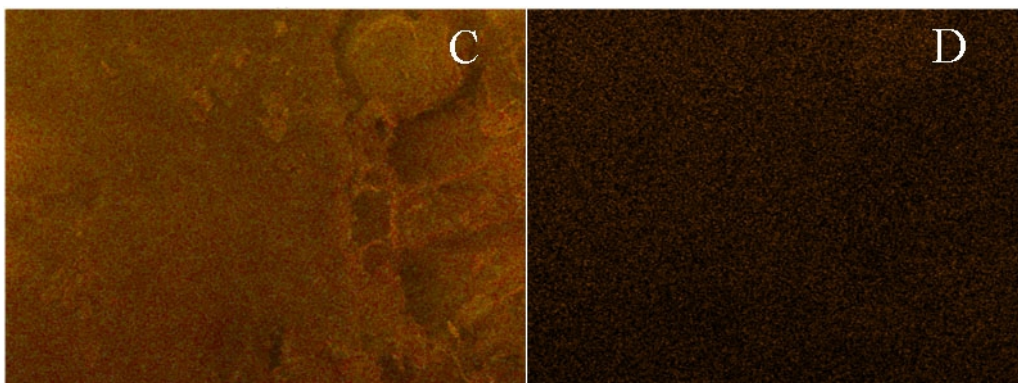


Fig. 3. X-ray diffraction patterns of  $\text{CeO}_2$  on  $\gamma$ - $\text{Al}_2\text{O}_3$  support.

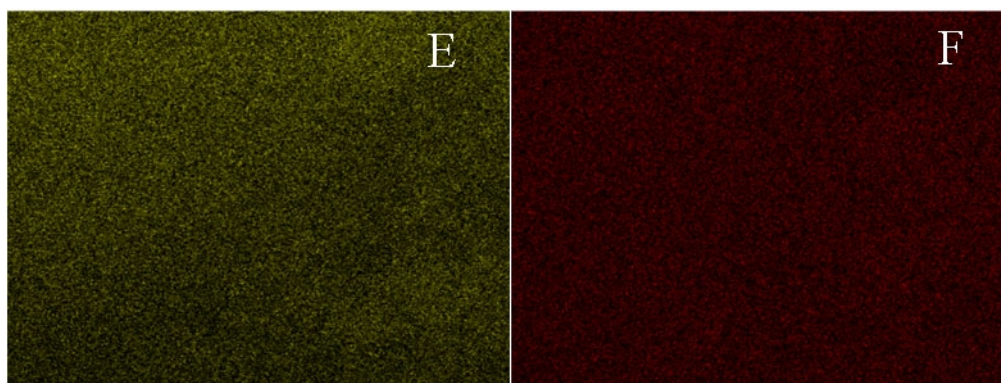
Fig. 1 and Fig. 2 presents the XRD patterns of  $\gamma$ - $\text{Al}_2\text{O}_3$  with different residence time in the hot zone or at different pyrolysis temperatures. With the particle residence time in hot zone is greater than 2.6 seconds,  $\gamma$ - $\text{Al}_2\text{O}_3$  characteristics of diffraction peaks were observed. As the pyrolysis temperature are 1000°C and 1100°C, their patterns peaks are identified as  $\gamma$ - $\text{Al}_2\text{O}_3$  peaks at 19.44°, 37.59°, 39.47°, 45.84° and 67.00°. When the pyrolysis temperature is down to 1173 K, there is no apparent crystalline phase corresponding to the sharp  $\gamma$ - $\text{Al}_2\text{O}_3$  peak, indicating that this sample have a certain percentages of the amorphous structure. Fig. 3 shows the  $\text{CeO}_2$  on  $\gamma$ - $\text{Al}_2\text{O}_3$  support, due to the  $\gamma$ - $\text{Al}_2\text{O}_3$  for broad diffuse peaks, so in the XRD patterns (Fig. 3) mainly display  $\text{CeO}_2$  patterns peaks (28.55°, 33.16°, 47.51°, 56.52°, 67.28°, 69.58°, 73.74°, 79.04°).





(C) SEM-EDS plane scan analysis

(D) Al element



(E) O element

(F) Ce element

Fig. 4. SEM-EDS plane scan analysis of CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

SEM image of synthesized CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support are shown in Fig. 4, the particles of cerium oxide can be found among pieces of alumina support with hollow spherical or irregular sheet (particle size of around 5~20  $\mu$ m). CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support in Fig. 4.(C, D, E, F) was analyzed with plane scan, mass fractions of chemical elements (mass, %): Al 35.6, O 32.9, Ce 31.5. The SEM-EDS plane scan analysis shows that CeO<sub>2</sub> has been formed successfully on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support and has uniform distribution and particles provide more reactive and reducible sites and results to a high catalytic performance of the catalyst. Furthermore, this kind of Al<sub>2</sub>O<sub>3</sub> has the advantage of ceria promoter with the wide area scale particles deposited on an inexpensive high surface area support that makes it a very suitable catalyst for VOC removal.

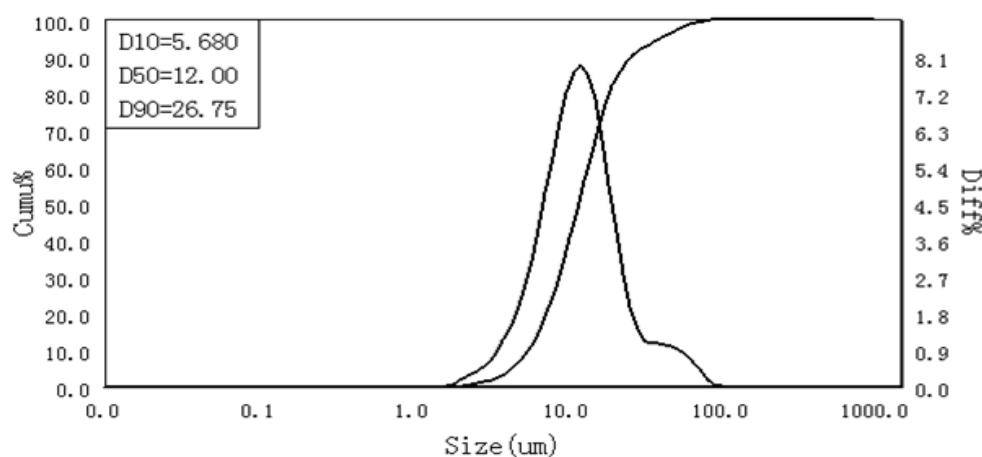


Fig. 5. Particle size distributions of CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

Fig. 5. shows particle size distributions of CeO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, there are approached to

high density compositions according to the size of 5.68~26.75  $\mu\text{m}$  and presents a high peaks, account for 77.25% of the total. The average particle size about 12.00  $\mu\text{m}$ . With ion selective electrode method for determination of chloride ion in the product, the content of chlorine ion is 0.13%.

## CONCLUSIONS

Synthesis of  $\text{CeO}_2$  on  $\gamma\text{-Al}_2\text{O}_3$  support by spray pyrolysis, With metal chloride as raw materials , the vast majority of rare earth products in the industrial production exists in the form of rare earth chloride and fluoride. The obtained  $\text{CeO}_2$  on  $\gamma\text{-Al}_2\text{O}_3$  support with a narrow particle size distribution, accounting for 77.25% of the particles have a distribution of between 5.68 ~ 26.75  $\mu\text{m}$ , the hollow spherical or flake has high specific surface area, and cerium oxide is uniformly distributed on the  $\gamma\text{-Al}_2\text{O}_3$ , this method is suitable for the preparation of VOCs catalyst.

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