Supporting Information

CeO_2 modified monolithic ceramic foams for efficient catalytic ozonation of refractory organic pollutants in a continuous-flow reactor

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The preparation parameters including the loading of γ-Al_2O_3 coating, calcination temperature, calcination time, and loading of CeO_2 were optimized.

Loading of γ-Al_2O_3 coating on CF

CF is a good monolithic support, but has different physical properties with active catalytic components. In order to strengthen the adhesion of active components and increase the surface area, γ-Al_2O_3 was selected as coating material before loading of CeO_2 because of its close property with α-Al_2O_3 CF and high porosity. The effect of γ-Al_2O_3 loading on the catalytic performance was investigated by repeated coating and calcination process of aluminum sol while the mass of CeO_2 was kept constant at 3.6wt%. Four catalysts with different γ-Al_2O_3 coating loads were noted as CeO_2/6%AlCF, CeO_2/13%AlCF, CeO_2/20%AlCF, and CeO_2/26%AlCF, respectively, while the percentage means the mass percentage of γ-Al_2O_3 on the CF support.

As shown in Fig. S1, the removal of TOC increased from 88.9% to 96.2% when the content of γ-Al_2O_3 increased from 13% to 20%. It was found from the BET analysis that γ-Al_2O_3 sol coating on CF support could form a porous structure after calcination, and the specific surface area increased from 0.684 m^2 g^{-1} to 97.2 m^2 g^{-1} with a transformation from a microporous surface to a mesoporous surface. The large specific surface area facilitates the loading and dispersion of Ce, providing more active sites for the catalytic ozonation. But when the mass of γ-Al_2O_3 increased further, TOC declined slightly to 93.3%. It was found that the excessive γ-Al_2O_3 tend to loss during the reaction, and the mass loss of the γ-Al_2O_3 and CeO_2 on the surface of the four monolithic catalysts were 0.5%, 0.9%, 1.3% and 2.4%, respectively, after 20 min of ultrasonication.

Calcination Temperature

When the calcination temperature is too low, the metal salt can not be completely transformed into oxides. But if the calcination temperature is too high, the catalyst will sinter and the active sites and accessible adsorption sites will be reduced. The calcination temperature was optimized ranged from 350 °C to 500 °C. The best catalytic performance was observed at a calcination temperature of 400 °C with TOC removal of 95.1% in 100 min, while the TOC removal was only 81.2% with a calcination temperature of 350 °C.

Calcination Time

Fig. S4 showed the effect of calcination time on the TOC removal. When the calcination time was set as 2 h, the removal rate of TOC was only 80.5%, which may be due to the incomplete decomposition of metal nitrate on the surface and the insufficient active sites due to the short calcination time. When the calcination time was increased to 3 h and 4 h, the removal of TOC increased to 83.9% and 95.1%, showing a high catalytic activity. However, when the calcination time was extended to 5 h, the TOC removal decreased slightly. Therefore, 4 h was selected as the calcination time for the catalyst preparation.

Loading of CeO_2

Under the preparation conditions of calcination temperature of 400 °C and calcination time of 4 h, the effect of concentrations of $Ce(NO_3)_3$ impregnating solution on the mineralized phenol effect of CeO_2/AlCF was investigated. As shown in Figure 3.5, when the impregnating solution concentration was increased from 0.1 mol L^{-1} to 0.3 mol L^{-1}, the TOC removal rate of the catalyst increased from 77.6% to 96.3%, and the degradation efficiency was significantly improved. However, too high ion concentration will cause excessive adsorption of cerium nitrate on the support surface, occupying a large number of effective active sites, thereby reducing the specific surface area, the catalytic activity decreased to 93.2%, and the excessive cerium nitrate caused sintering after high-temperature calcination reduced the porosity and even blocked the pores, affecting the mass transfer effect. Considering the economy, environmental protection and catalytic activity, the concentration of impregnation solution is selected as 0.3 mol L^{-1}.

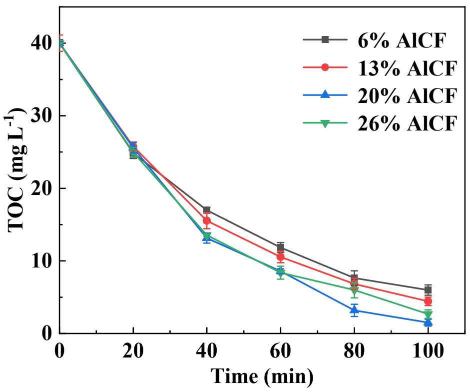

Fig. S1 Effect of γ-Al_2O_3 loading on TOC removal of phenol (Conditions: calcination temperature 400 °C, calcination time 4 h, concentration of $Ce(NO_3)_3$ impregnating solution 0.3 mol L^{-1}, $[O_3]$ =10.1 mg L^{-1}, pH =7.2)

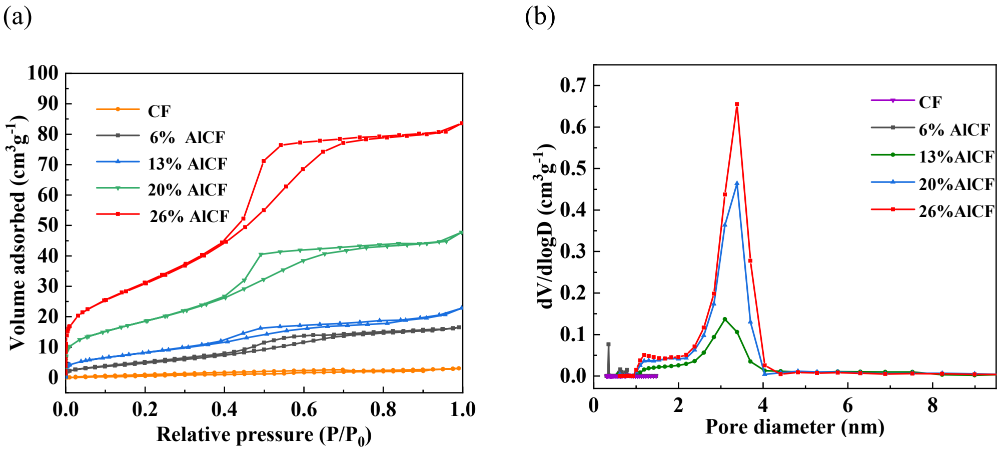

Fig. S2 (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of different AlCF

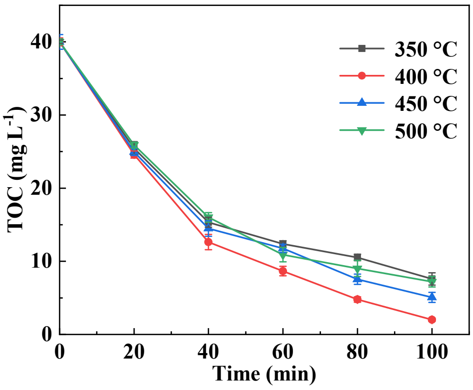

Fig. S3 Effect of calcination temperature on TOC removal of phenol (Conditions: calcination time 4 h, concentration of $Ce(NO_3)_3$ impregnating solution 0.3 mol L^{-1}, $[O_3]$ =10.1 mg L^{-1}, pH =7.2)

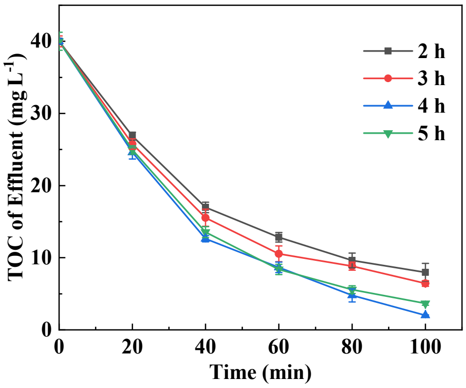

Fig. S4 Effect of calcination time on TOC removal of phenol (Conditions: calcination temperature 400 °C, concentration of $Ce(NO_3)_3$ impregnating solution 0.3 mol L^{-1}, $[O_3]$ =10.1 mg L^{-1}, pH = 7.2)

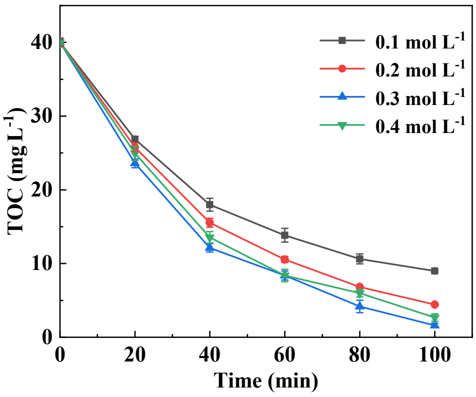

Fig. S5 Effect of concentration of impregnation solution on TOC removal of phenol (Conditions: calcination temperature 400 °C, calcination time 4 h, $[O_3]$ =10.1 mg L^{-1}, pH =7.2)

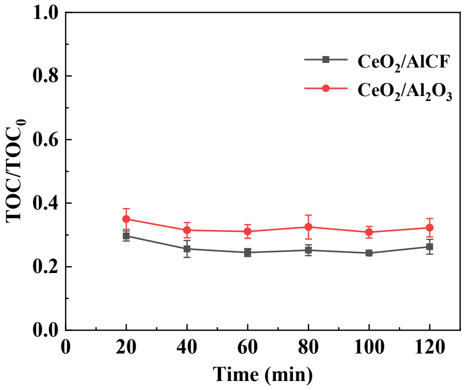

Fig. S6 Effect of CeO_2/AlCF and CeO_2/Al_2O_3 on TOC removal of phenol (Conditions: Catalyst dosage=60 g L^{-1}, [phenol]=40 mg L^{-1}, initial pH=7, HRT=12 min, $[O_3]$ =20.2 mg L^{-1}, pore density=30 ppi)

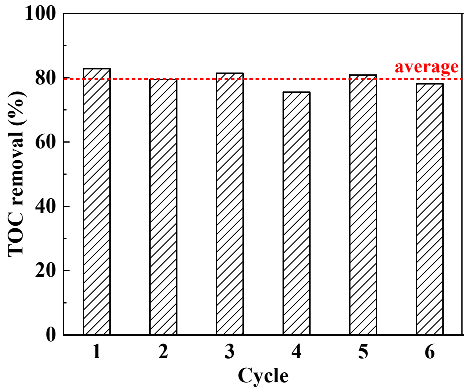

Fig. S7 Stability of phenol degradation by CeO_2/AlCF

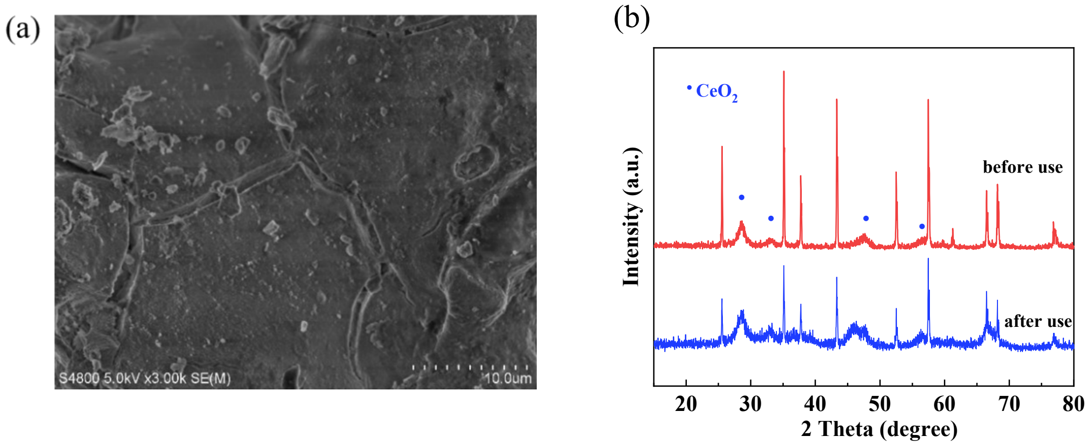

Fig. S8 (a) SEM and (b) XRD of CeO_2/AlCF after catalytic reaction

Table S1 Specific surface area, pore volume and pore diameter of AlCF with different coating content

Catalysts	Specific surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
CF	0.684	0.001	0.349
6%AlCF	17.7	0.005	0.349
13%AlCF	24.8	0.030	3.099
20% AlCF	68.2	0.093	3.385
26% AlCF	97.2	0.121	3.385

Table S2 Water quality of effluent from the secondary sedimentation tank of a petrochemical wastewater treatment plant for practical wastewater treatment

Index	value
pH	8.6
Chemical Oxygen Demand (COD) (mg/L)	136
Total Organic Carbon (TOC) (mg/L)	51.1
NH_4^+-N (mg/L)	3.5
Conductivity (μS/cm)	3900