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Catalytic Ozonation of Atrazine Enhanced by Mesoporous CeO$_2$: Morphology, Performance and Intermediates

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Abstract: Heterogeneous catalytic ozonation is an alternative approach for the removal of refractory pollutants from water, and the fabrication of mesoporous materials with high dispersibility would enhance the catalytic efficiency. A mesoporous CeO$_2$ was prepared by the nanocasting method with SBA-15 as a hard template, and was investigated in the catalytic ozonation of atrazine. The synthetical CeO$_2$ nanorods have a specific surface area of 95.08 m^2/g, a diameter of 10.16 nm, and a spacing of 2.18 nm. The removal rate of atrazine was 85.5%, 64.8%, and 46.4% in the order of catalytic ozonation by synthetical CeO$_2$ > single ozonation > catalytic ozonation by commercial CeO$_2$, respectively. The superior activity of the synthetical CeO$_2$ could be attributed to the well-ordered mesoporous structure, the high surface area, and the redox Ce^{3+}/Ce^{4+} cycling. Moreover, eight organic intermediates were identified after one minute of catalytic ozonation of atrazine, and the cleavage of the ethylamino group was proposed as the main pathway of atrazine degradation.

Keywords: catalytic ozonation; atrazine; CeO$_2$; mesoporous

1. Introduction

Atrazine as a chlorinated triazine herbicide has been widely used in agriculture, especially for the control of crops and grassy weeds [1]. It has a water solubility of 33 mg L^{-1} at 25 °C, an organic carbon partition coefficient value of 100 L kg^{-1}, and a half-life ranging from 21 days to two years, which makes it possible to leach into the aquatic ecosystem and persist for a long time [2]. Atrazine, even at low concentrations in water bodies, could cause serious negative effects on human health through the accumulation of it in the food chain [3], and has been listed as a priority substance by the European Commission. Notably, the detected concentration of atrazine in surface water and groundwater in Beijing ranged from 0.12 to 5.16 µg L^{-1}, which exceeded the allowable level of 3 µg L^{-1} for drinking water [4]. However, the traditional water purification methods are obviously not enough to remove atrazine from water efficiently and completely [5], and the by-products such as halogens might cause a more serious ecological impact [6]. Therefore, it is an urgent requirement to develop an effective removal method for reducing its environmental exposure.

Besides persulfate oxidation [7], photocatalytic oxidation [8], and electrochemical oxidation [9], heterogeneous catalytic ozonation technology is a promising technology for the removal of refractory pollutants [10], which could generate highly reactive hydroxyl radicals with a redox potential of 2.80 eV and rapidly and non-selectively degrade or even mineralize antibiotics with 10^6–10^{10} L mol^{-1} s^{-1} reaction rate [11]. Li et al. [12] evaluated the degradation of atrazine by the catalytic ozonation of iron scraps, and the results showed that the mineralization efficiency was as high as 86.6%, and the toxicity was efficiently

removed at 30 min. Ye et al. [13] identified that the prepared catalyst could effectively improve the degradation and mineralization rate of atrazine, and the mineralization strongly depended on the solution's pH. Zeghioud et al. [14] concluded that catalytic ozonation coupled with discharge plasma could improve the removal efficiency of refractory organic pollutants. He et al. [15] combined membrane filtration and catalytic ozonation for the removal of atrazine, 99.99% of atrazine could be removed within 40 min and hydroxyl radicals were inferred to be the main reactive oxygen species in the catalytic ozonation process. Three pollutant degradation pathways are normally proposed in the process of heterogeneous catalytic ozonation [16]. Firstly, ozone is adsorbed on the catalyst surface and catalyzed to generate radical oxygen species, which further degrades the organic pollutant adsorbed on the catalyst surface or in solution. Secondly, ozone directly attacks and degrades the organic pollutants adsorbed on the surface of the catalyst or the complex formed by organic pollutants and the catalyst. Thirdly, both ozone and organic pollutants are simultaneously adsorbed and reacted on the surface of the catalyst. Obviously, heterogeneous catalytic processes are really complicated, involving gas phase (ozone), liquid phase (water) and solid phase (catalyst), where catalysts would perform various roles, such as providing active sites for adsorption and catalytic ozonation. Therefore, the textural properties of catalysts, such as surface area, pore volume and porosity, are the keys to catalytic efficiency.

Numerous studies have been devoted to designing and optimizing the properties of catalysts to improve the efficiency of catalytic ozonation. Bing et al. [17] prepared Fe_2O_3/Al_2O_3@SBA-15 by wet impregnation and calcination, and characterized that Al_2O_3 and Fe_2O_3 were highly dispersed on SBA-15, and amounts of surface Lewis acid sites existed due to the substitution of Al^{3+} for the hydrogen of Si-OH. Yuan et al. [18] synthesized microporous iron silicate with poor crystallinity and found that Fe-Si binary oxides inhibited the futile decomposition of ozone and increased the probability of hydroxyl radicals generated through the reaction between ozone and α-Fe_2O_3. Our previous work prepared a mesoporous MnO_2 by the nanocasting method and found that the ordered nanorods with a high surface area facilitated mass transport and exposure of active sites [19]. Besides MnO_2, CeO_2 is another widely studied heterogeneous catalyst for catalytic ozonation. The cerium redox pair (Ce(III) and Ce(IV)) performs a synergetic effect on catalytic ozonation, where Ce(III) could catalyze ozonolysis to generate hydroxyl radicals and would be regenerated through the reduction of Ce(IV) [20]. Notably, the surface basicity, defect density/oxygen vacancies and unsaturated coordination sites of CeO_2 crystal planes exposed are important factors in the catalytic performance, such as the ability of different crystal planes in the order of (100 + 110) > (100) > (111) to enhance the mineralization of nitrophenol [21].

In this study, an ordered mesoporous CeO_2 with a high surface area was prepared with SBA-15 as the hard template by the nanocasting method and used as an efficient catalyst for catalytic ozonation of atrazine. The textural properties of the synthesized samples were characterized by X-ray diffraction(XRD), surface area analysis techniques, scanning electron microscope (SEM), transmission electron microscope (TEM), and X-ray photoelectron spectroscopy (XPS). The performance of CeO_2 was investigated by evaluating the degradation of atrazine under various conditions compared with control samples. Moreover, the degradation pathways were assessed through the identification of intermediate products. This study may provide an approach to effectively remove refractory pollutants in the process of wastewater treatment.

2. Materials and Methods

2.1. Materials

SBA-15 was purchased from XFNANO Co., Ltd. (Nanjing, China). The commercial CeO_2 and $Ce(NO_3)_3 \cdot 6H_2O$ were supplied by Sinoparm Chemical Reagent Co., Ltd. (Shanghai, China). Atrazine was provided by the laboratory of the government chemist (Germany). NaOH was purchased from Rhawn Reagent (Shanghai, China). H_2SO_4 was obtained from Yantai Far East Fine Chemical Co., Ltd. (Yantai, China). All chemicals

used were of analytical grade without further purification. Deionized water (18 MΩcm) produced by the Milli-Q purification system (Millipore, USA) was used to prepare solutions. Ozone was supplied by an ozone generator (COM-AD-01, ANSEROS), and the ozone stock solution was obtained by bubbling gaseous ozone into a 1 L cylindrical reactor filled with pure water for 30 min.

2.2. Preparation of CeO_2

The synthesis of mesoporous CeO_2 was based on a previously reported method [19]. Concisely, 4.51 g of SBA-15 was dispersed in an ethanol solution (15 mL of ultrapure water and 90 mL of ethanol) under stirring with a magnetic bar at room temperature. A total of 13 g of $Ce(NO_3)_3 \bullet 6H_2O$ was added into the suspended solution and kept stirring for 2 h. The solid was filtered from the suspension, dried for 5 h at 105 °C, and subsequently calcined at 300 °C for 3 h. The CeO_2/SBA-15 complex obtained was rinsed with 2M NaOH, then washed to neutral with ultrapure water and dried for 3 h at 105 °C.

2.3. Experimental Procedure

The experimental procedure was conducted in batch mode in a 0.6 L cylindrical reactor with a diameter of 80 mm and a height of 120 mm at room temperature. Basically, appropriate amounts of catalyst and atrazine stock solution were added to the reactor under continuous magnetic stirring. Then, appropriate ozone stock solutions were added to the reactor to initiate catalytic ozonation (the initial mixing solution contained 50 μg L^{-1} atrazine, 20 mg L^{-1} catalyst and 1 mg L^{-1} O_3). The solution of an appropriate volume was sampled from the reactor at certain intervals, filtered with a 0.22 μm prefilter and quenched with a trace of $Na_2S_2O_3$ for further analysis. Two samples were repeated for each experiment.

2.4. Characterization

The XRD patterns were recorded in the 2θ range of 5–60° using a Rigaku Ultima V diffractometer with Cu Kα as the radiation source. The surface area was measured on an automatic adsorption analyzer (ASAP2460, Micromeritics Instrument Corp., Norcross, GA, USA) and calculated by the Brunauer–Emmett–Teller (BET) method. The structure and morphology of the as-prepared CeO_2 were characterized by transmission electron microscopy (FEI Tecnai G2 F20, NL) and scanning electron microscopy (Zeiss Sigma 300, GER) equipped with an energy-dispersive spectrometer. The elementary compositions of the prepared samples were analyzed by X-ray photo-electron spectroscopy (Thermo Fisher Scientific, Waltham, MA, USA).

The atrazine concentration was detected by high-performance liquid chromatography (LC-20AT, Shimadzu, JPN) equipped with a diode array detector. A reversed-phase C18 column was used under isocratic elution with methanol and phosphoric acid solution (v/v, 55:45) at 1.0 mL/min at 35 °C. The intermediates were identified by an ultra-performance liquid chromatography tandem quadrupole time of flight mass spectrometer (LCMS-9030, Shimadzu). Gaseous O_3 concentrations were monitored using an ozone analyzer (GM-6000-OEM, ANSEROS). Aqueous O_3 concentrations were measured by iodometry and were calculated using the following equation.

$$C_{(O3)} = 24000 C_{(Na2S2O3)} V_{(Na2S2O3)} / V_{(O3)} \tag{1}$$

where $C_{(O3)}$ is the aqueous O_3 concentration, mg/L; $C_{(Na2S2O3)}$ is the concentration of $Na_2S_2O_3$ standard solution, mol/L; $V_{(Na2S2O3)}$ is the consumed volume of $Na_2S_2O_3$ standard solution, mL; $V_{(O3)}$ is the titration volume of the aqueous O_3, mL.

3. Results and Discussion

3.1. Characterization of CeO₂

The XRD patterns of the CeO_2 samples are shown in Figure 1. The synthetical and commercial samples both exhibited five distinguished diffraction peaks at 28°, 33°, 47°, 56° and 59°, which could be indexed to the (111), (200), (220), (311) and (222) reflection planes of CeO_2 (JCPDS No. 78-0694) [22]. The peaks of synthetical CeO_2 were wider and weaker than those of commercial CeO_2, which implied that the crystal size of synthetical CeO_2 was smaller than that of commercial CeO_2. The average crystal size of the synthetical and commercial CeO_2 was 9.8 nm and 37.4 nm, respectively, through the calculation of the Scherrer formula as below [23].

$$D = K\lambda/\beta\cos\theta \quad\quad\quad (2)$$

where D is the average crystal size; K is a constant of 0.89; λ is the X-ray wavelength of 0.154 nm; β is the full width at half maximum of the diffraction peak; θ is the diffraction angle.
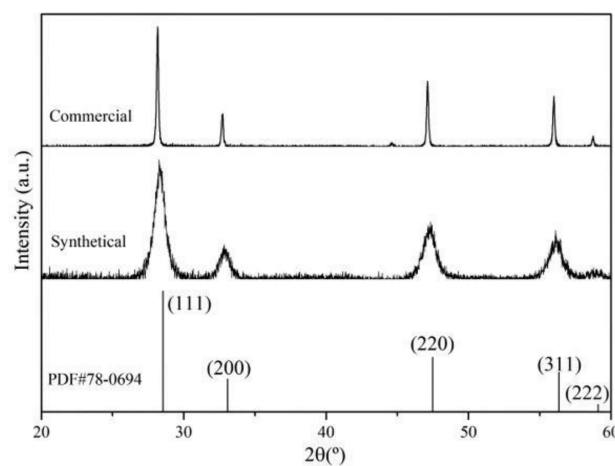

Figure 1. XRD pattern of CeO_2 samples.

The BET adsorption-desorption isotherms were measured to analyze the specific surface area and pore information of CeO_2. In Figure 2a, the hysteresis loop of the synthetical CeO_2 corresponded to type IV, indicating the existence of mesopores. The commercial CeO_2 might be nonporous or microporous since its hysteresis loop belonged to type I. Moreover, the specific surface area of the synthetical and commercial CeO_2 shown in Table S1 was 95.08 m^2/g and 1.44 m^2/g, respectively, and the specific surface area of the synthetical CeO_2 was significantly higher than that of the commercial CeO_2, which implied that the synthetical CeO_2 would provide more catalytic sites and facilitate catalytic ozonation as it could offer more active site exposure possibilities compared to the commercial CeO_2 of the same mass. Figure 2b showed that the synthetical CeO_2 had a relatively concentrated pore distribution while the commercial CeO_2 was almost non-porous, which echoed the analysis of BET adsorption-desorption isotherms and implied that the synthetical CeO_2 might be of ordered mesopores.

The morphologies of CeO_2 were characterized by SEM, and the images are shown in Figure 3. Apparently, the CeO_2 samples presented different degrees of aggregated morphology, and the synthetical CeO_2 seen in Figure 3a,c exhibited granular while the commercial CeO_2 seen in Figure 3b,d exhibited layered, which implied that the surface area of synthetical CeO_2 would be much higher than that of commercial CeO_2. Figure 4 displays the TEM images of CeO_2 within different nanometer dimensions. Through the comparison of samples, the synthetical CeO_2 exhibited higher dispersibility than the commercial CeO_2, which was consistent with the SEM results. Moreover, the synthetical CeO_2 was a nanorod with well-ordered channels, while the commercial CeO_2 was a nanocube with high agglomeration. Further, the nanorod was 10.16 nm in diameter, and

the distance between each channel was 2.18 nm, implying the synthetical CeO_2 had an ordered mesoporous structure and would have large active sites exposed. The synthetical CeO_2 dominantly exposed (111) facets with an interplanar spacing of 0.31 nm, while the commercial CeO_2 mainly exposed (200) facets with an interplanar spacing of 0.19 nm. The lattice fringes revealed the high crystallinity of CeO_2, which further proved the results of XRD.
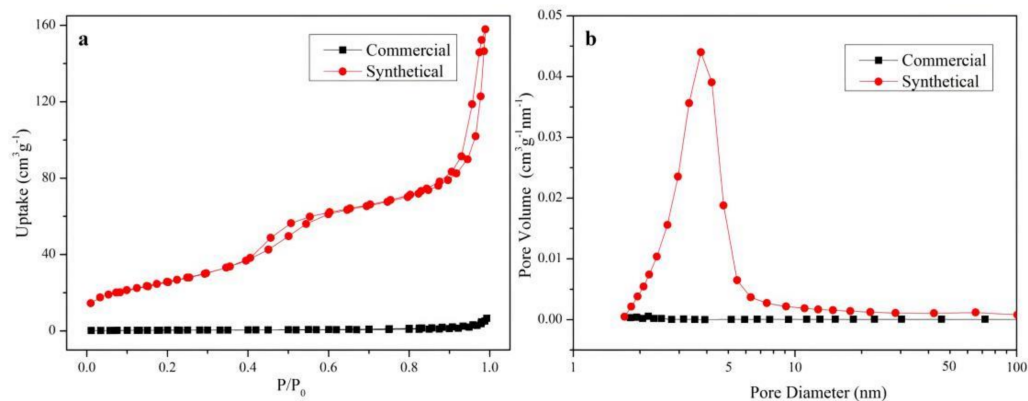

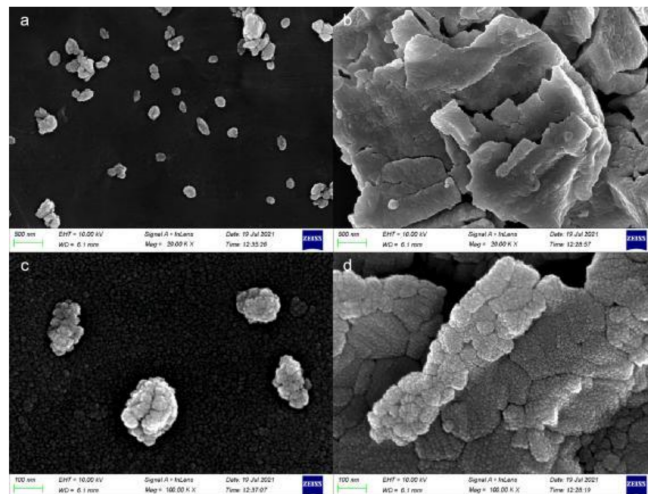**Figure 2.** Nitrogen adsorption-desorption isotherms (**a**) and pore size distribution (**b**) of CeO_2.

Figure 3. SEM images of synthetical (**a**,**c**) and commercial (**b**,**d**) CeO_2.
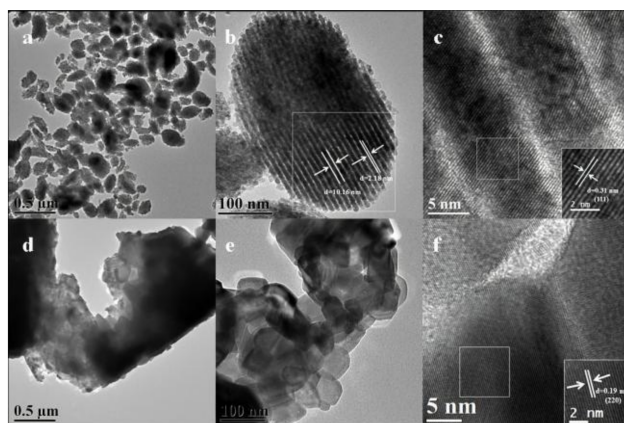

Figure 4. TEM images of synthetical (**a**–**c**) and commercial (**d**–**f**) CeO_2 within different nanometer dimensions.

The redox couple between Ce^{3+}/Ce^{4+} or O^{2-}/O_3 plays a crucial role in enhancing the catalytic activity as the electrons from Ce^{3+} would be transferred to O_3, which decomposes O_3 into reactive oxygen species, and the electrons from O^{2-} would reduce the Ce^{4+} to Ce^{3+} [21]. The chemical states of Ce/O and their concentrations on the sample surface were analyzed from the XPS spectra. As illustrated in Figure 5a, the Ce 3d XPS spectra consisted of two series of spin-orbit lines, where v represented the Ce 3d3/2 spin-orbit splitting peak while u represented the Ce 3d5/2 spin-orbit splitting peak. The spin-orbit was well-fitted with ten peaks through deconvolution [24], and the energy positions of these ten spin-orbit components were summarized in Table S2. Taking the synthetical sample as an example, three pairs of peaks, including v (882.46 eV) and u (900.98 eV), v″ (888.87 eV) and u″ (907.61 eV), and v‴(898.18 eV) and u‴ (916.83 eV), were related to the characteristic peaks of Ce^{4+}. The remaining two pairs of peaks marked as v_0 (880.38 eV) and u_0 (898.38 eV) and v′ (884.84 eV) and u′ (903.05 eV) belonged to the characteristic peaks of Ce^{3+} [24]. The results indicated that cerium existed in CeO_2 in two valence states [25], Ce^{3+} and Ce^{4+}, and the atomic ratio of Ce^{3+} to Ce^{4+} was 10.14% and 12.59% for the synthetic and commercial CeO_2, respectively. The emergence of multivalent cerium would facilitate the charge transfer and the production of reactive oxygen species during the catalytic ozone process. The presence of Ce^{3+} would introduce the occurrence of oxygen vacancies on CeO_2. As illustrated in Figure 5b, the O 1s XPS spectra exhibited a strong peak with a shoulder, and might be related to four kinds of surface oxygen states. The fitting peak at 529.47–529.51 eV could be attributed to the lattice oxygenis [26], the one at 530.51 eV could be assigned as the surface oxygen from the hydroxyl group [27], and the adjacent peaks at 531.46–531.47 eV and 531.81–531.97 eV should be characteristic of subsurface O^-/O_2^{2-} species, which belong to oxygen substances chemically adsorbed at oxygen vacancies and would improve the catalytic activity [28].
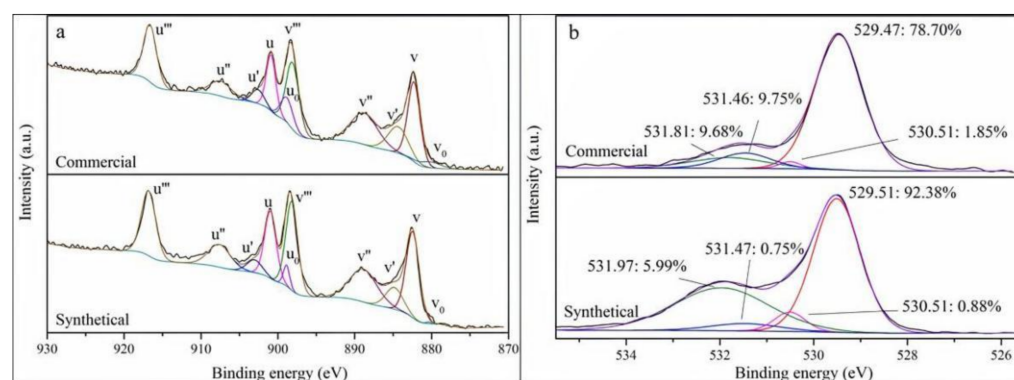

Figure 5. XPS spectra of Ce 3d (**a**) and O 1s (**b**) of CeO_2..

3.2. Catalytic Ozonation of Atrazine

To evaluate the catalytic superiority of the synthetical CeO_2 for ozonation, the atrazine degradation experiments were carried out under different conditions. The adsorption was performed for 10 min before atrazine degradation. As shown in Figure 6a, the adsorption amount of synthetical CeO_2 was as high as 9.9%, while that of the commercial one was only 4.0%. The good adsorption capacity is attributed to the high surface area of synthetical CeO_2, which would be favorable for the reaction of atrazine with hydroxyl radical generated on the catalyst surface. The atrazine removal rate with synthetical CeO_2 could reach up to 85.5% after 10 min, while the removal rates with commercial CeO_2 and ozone alone were 64.8% and 46.4%, respectively. The performance of synthetical CeO_2 on catalytic ozonation of atrazine was statistically ($p < 0.05$) different from and better than that of commercial CeO_2 or ozone alone, indicating that the synthetical CeO_2 effectively enhanced the catalytic ozonation and its catalytic activity was obviously superior to commercial CeO_2. The nano-ZnO [29] and mesoporous Fe_3O_4 [30] were also prepared as ozonation

catalysts to enhance the degradation of atrazine, and in contrast, the synthetical CeO_2 could obtain the high removal efficiency of atrazine at a dose of less than an order of magnitude. To further quantitatively analyze the catalytic activity of CeO_2, the rate constants were calculated according to the pseudo-first-order kinetic equation [13]:

$$-\ln(C_t/C_0) = k_{obs}t \qquad (3)$$

where C_t is the atrazine concentration at the reaction time t, C_0 is the initial atrazine concentration, and k_{obs} is the pseudo-first-order constant. As shown in Figure 6b, the apparent rate constant for ozone alone was 0.074 min^{-1}, while the apparent rate constant increased to 0.175 min^{-1} and 0.097 min^{-1} after the addition of synthetical and commercial CeO_2, which demonstrated that the applied CeO_2 could promote the removal of atrazine. Notably, the apparent rate constant of synthetical CeO_2 was significantly higher than that of commercial CeO_2, which was associated with the superior aforementioned properties such as mesoporous structure, high surface area, as well as good dispersibility.
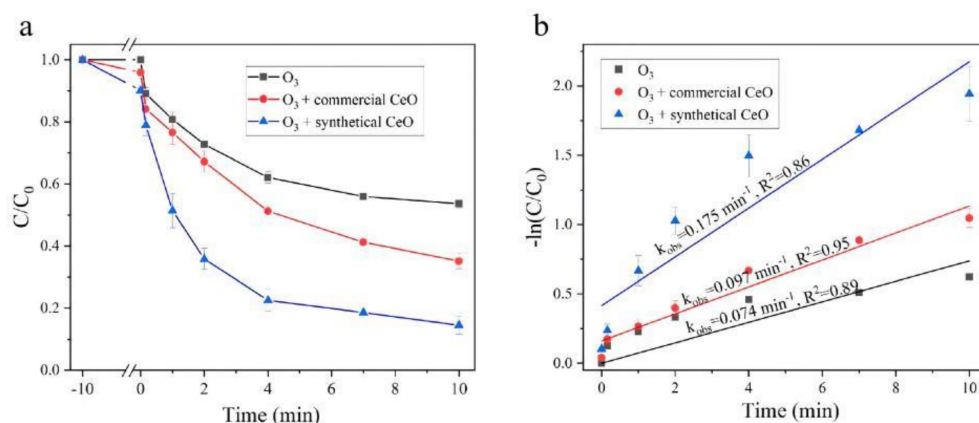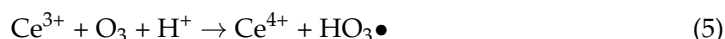

Figure 6. The curves (**a**) and pseudo-first-order plots (**b**) of atrazine degradation in different processes (atrazine concentration = 50 µg/L; catalyst dose = 20 mg/L; ozone concentration = 1 mg/L; initial pH = 7).

Combined with the experimental results and previous research [31], the atrazine degradation was a relatively complex process during the catalytic ozonation, which included adsorption, direct oxidation by molecular ozone and indirect oxidation by hydroxyl radical. The catalytic mechanism of synthetical CeO_2 on the ozonation of atrazine could be summarized as follows:

$$CeO_2 + Atrazine_{(aqu)} \rightarrow CeO_2 \equiv Atrazine_{(ads)} \qquad (4)$$

$$Ce^{3+} + O_3 + H^+ \rightarrow Ce^{4+} + HO_3\bullet \qquad (5)$$

$$HO_3\bullet \rightarrow \bullet OH + O_2 \qquad (6)$$

$$\bullet OH + O_3 \rightarrow O_2{}^- + HO_2\bullet \qquad (7)$$

$$O_2{}^- + O_3 \rightarrow O_3{}^- + O_2 \qquad (8)$$

$$O_3{}^- + H^+ \rightarrow HO_3\bullet \qquad (9)$$

$$HO_3\bullet \rightarrow \bullet OH + O_2 \qquad (10)$$

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad (11)$$

$$\bullet OH + CeO_2 \equiv Atrazine_{(ads)} \rightarrow byproducts \qquad (12)$$

The pH value has an important influence on the chemical characteristics of the catalyst surface, the charge of ionic organic molecules, and the decomposition of O_3 into reactive oxygen species in the catalytic process [32]. The influence of the initial pH value on the catalytic efficiency would be taken into account in the subsequent evaluation of the environmental influence on the catalytic performance.

3.3. Transformation Products and Proposed Pathways

The molecular structure of atrazine mainly consists of the s-triazine ring, the isopropylamino group, the ethylamino group and the chlorine group, and the nitrogen atom in the amino group and the chlorine atom adjacent to the s-triazine ring are vulnerable to radical oxygen species [15]. It is widely recognized that the degradation of atrazine in catalytic ozonation involves the reaction pathways: dealkylation, dechlorination, deamination and olefination [33]. However, the priority of the pathways was basically not involved in previous studies on reaction pathways since the sampling time for the determination of intermediates was not considered.

The previous results shown in Figure 5a indicated that atrazine could be mostly degraded within 10 min, and half could be degraded in one minute. The sample after one minute of catalytic ozonation could better reflect the early reaction process and was used for the determination of intermediates. Eight organic intermediates with m/z values of 232, 174, 214, 230, 172, 212, 188 and 146 were successfully identified (mass error within 0.5 ppm), and were shown in Table S3 and Figure S1. Based on the intermediates and literature reports, the degradation pathway for the catalytic ozonation of atrazine was proposed in Figure 7. Apparently, the structural changes of atrazine first occurred in the isopropylamino and ethylamino groups. Six intermediate products were detected during the change of the ethylamino group, and their mass spectral peak responses were relatively higher, which could be inferred that the change of the ethylamino group was the main pathway of atrazine degradation. The ethylamino group was attacked by hydroxyl radicals to form the hydroxylated intermediate P1(m/z = 232), and the formed hydroxyl group could be easily attracted to form carbon-centered radicals, which could further add oxygen and rapidly eliminate hydroxyl peroxide radical to generate ketones P4(m/z = 230) [34], and further attacked by hydroxyl radicals, leading to the loss of chlorine and the formation of hydroxylated intermediate P6(m/z = 212). The intermediate P3(m/z = 232) was formed from the olefination of P1, followed by further dealkylation to form the intermediate P5(m/z = 172) [35]. It is noted that the dealkylation reactions were ubiquitous, and the intermediates P2(m/z = 174), P5, P7 and P8(m/z = 146) were the products of dealkylation reactions since the nitrogen atoms on the isopropylamino group and ethylamino group were prone to being attacked, resulting in the heterolytic cleavage of the C–N bond [15]. These intermediates were also observed in other advanced oxidation processes, such as photocatalytic oxidation, persulfate oxidation and Fenton oxidation. All the above intermediates would be further oxidized to low molecular organics and even mineralized to CO_2 and H_2O by prolonging the reaction time, which was widely investigated in previous studies [29]. The results indicated that the initiating reaction of catalytic ozonation of atrazine mainly occurred on the ethylamino group and proceeded to the dealkylation reactions.
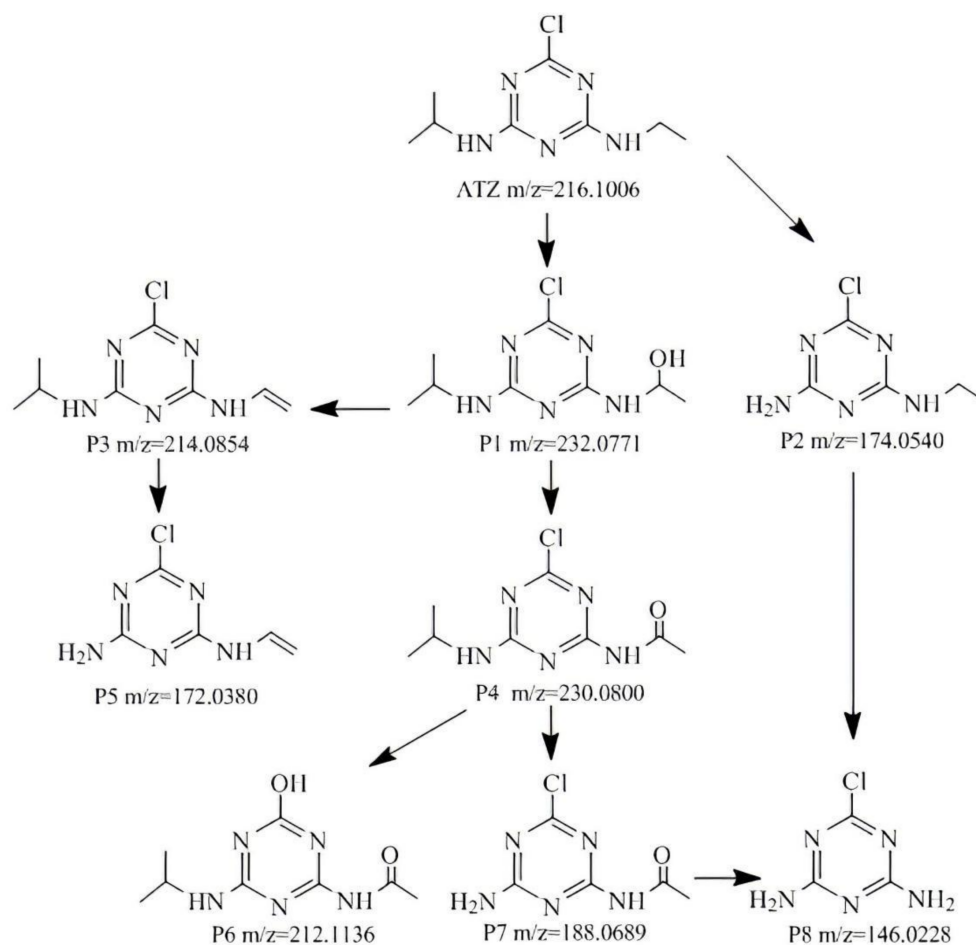
Figure 7. Proposed degradation pathway of atrazine.

4. Conclusions

The mesoporous CeO$_2$ was successfully obtained by the nanocasting method and investigated for catalytic ozonation of atrazine. Compared with commercial CeO$_2$ and single ozone, synthetical CeO$_2$ significantly enhanced the removal of atrazine due to its excellent properties such as high surface area, well-ordered mesoporous structure and redox Ce^{3+}/Ce^{4+} couple. Eight organic intermediates were identified, and the initiating reaction of catalytic ozonation of atrazine mainly occurred on the ethylamino group, followed by the dealkylation reactions. This study might facilitate the application of mesoporous metal oxide and the understanding of the degradation pathways of organic pollutants in catalytic ozonation.

Author Contributions: J.Z.: Methodology, Software, Investigation, Writing-original draft; T.Z.: Writing—review & editing, Supervision, Data curation; S.L.: Investigation, Writing—review & editing; S.S.: Software, Writing—review & editing; Y.W.: Writing—review & editing; X.L.: Writing—review & editing; J.W.: Writing—review & editing; R.L.: Resources, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

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