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Effect of Pd/Ce Loading and Catalyst Components on the Catalytic Abatement of Toluene

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Abstract: Monolithic catalysts are widely used in industrial catalysis. However, in the preparation of a monolithic catalyst, the traditional methods have some drawbacks such as low washcoat uploading ratio and poor uniformity. In the present work, the effects of Pd/Ce loading and catalyst components on the catalytic abatement of toluene were investigated. The acid treatment of the substrate, the particle size of the slurry and the dispersant on the uniformity of the washcoat and the catalytic performance were also explored. Characterisation was achieved via BET, SEM, zeta potential and laser grain-size analyses. The results showed that the catalytic activity of the catalyst increased with the increasing of the Ce content. It was found that the 0.2Pd-0.3Ce/ γ -Al₂O₃ catalysts had the best toluene catalytic activity. The pretreatment of the cordierite with 20% HCl could improve the properties of the cordierite. It was also found that reducing the particle size of the washcoat and adding dispersant PAA could effectively improve the stability of the suspension and the uniformity of the washcoat. When 20% HCl pretreatment was used, the toluene catalytic activity of the monolith catalyst prepared by cordierite increased, in which T₁₀ and T₉₀ decreased by about 5 °C. Decreasing the particle size and dispersant also promoted the efficiency of catalytic degradation.

Keywords: Pd; CeO₂; monolithic catalyst; catalytic performance



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1. Introduction

The rapid development of industry has complicated the types of Volatile Organic Compounds (VOCs) emitted [1]. Of the current VOC removal processes, catalytic combustion is one of the more mature and widely used technologies. It transforms VOCs into pollution-free substances at low temperatures through the action of a catalyst [2]. In practical industrial applications, monolithic catalysts are widely used because of their lower bed pressure [3], and superior interphase mass transfer [4] and heat transfer [5] performance, as compared with powder catalysts. In general, the monolithic catalyst includes the active phase, the washcoat and the substrate.

Precious metal catalysts and transition metal oxide catalysts are usually used as the active phase in the catalyst. Pd-based catalyst has been widely considered because of its low starting temperature, high selectivity, high removal rate and so on [6,7]. Furthermore, doping a certain amount of rare earth elements into the catalyst can obviously improve the dispersion and anti-sintering ability of the active component, enhance the binding strength between the carrier and the active component, and improve the catalytic activity of the catalyst [8]. The rare earth element cerium (Ce) has been widely used in catalysis in recent years. However, there are few studies on the effects of bimetallic catalyst compositions, precious metal contents, and rare earth metals on the activity of precious metal catalysts.

Currently, honeycomb ceramics are commonly used as substrates of integral catalysts; these have the advantages of regular shape and high mechanical strength [9]. As one of the commonly used carriers for monolithic catalysts, cordierite ceramics have excellent

mechanical strength and thermal expansion coefficients, but also have problems such as surface impurities that lead to the blockage of carrier channels and a small specific surface area ($<1 \text{ m}^2/\text{g}$), which result in a low catalyst loading ratio [10–12]. To obtain a larger specific surface area, commonly used methods include: (1) preparation of a washcoat by loading a carrier with a high specific surface area on the surface of the substrate [13–16]; (2) acid treatment of the cordierite surface [17–19]. At present, alumina, titanium dioxide, and molecular sieves are the most commonly used as the washcoat. Lai et al. [20] used alumina as the coating substrate support to prepare a $\text{MnO}_x/\text{La-Al}_2\text{O}_3$ monolithic catalyst by the incipient wetness impregnation method, with a T_{90} of 275°C for the catalytic degradation of toluene. Yang et al. [21] used OMS-2 as the coating substrate support to prepare a $\text{Co}_3\text{O}_4/\text{OMS-2}$ monolithic catalyst, resulting in the contact area of an equivalent mass of catalyst increasing approximately four-fold compared with the traditional powder-type catalyst. Lu [22] and Sun [23] used different concentrations of nitric acid for acid pretreatment of the carrier, which not only improved the specific surface area of the carrier but also increased the loading ratio of the coating, thus improving the catalytic performance of the monolithic catalyst. Therefore, the performance of the monolithic catalyst obtained by acid pretreatment of the carrier was better than that obtained by adjusting the proportions of the slurry. Although substrate pretreatment is closely related to the active phase upload and the service life of the monolithic catalyst [24], there are few reports on the substrate treatment system [25]. A uniform washcoat plays an important role in the catalytic reaction and the stability of the slurry is important to obtain a uniform washcoat [26]. To obtain a stable slurry, the particles in the slurry need to disperse effectively, which depends on the net charge on the surface of the particle [27]. Given this, it is necessary to systematically study the pretreatment of the monolithic catalyst carrier and the dispersion performance of the catalyst slurry to prepare monolith catalysts with uniform washcoats and high catalytic efficiencies.

In the present study, $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Pd-Ce}/\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared by equal volume impregnation method to investigate the effect of CeO_2 doping on the catalytic oxidation of toluene. The treatment effects of different types of acids on the surface of cordierite substrates under different conditions were explored. The pretreatment process was optimised and screened to improve the specific surface area of the cordierite substrate to improve its performance. The influence of the ball milling conditions on the size of the washcoat and the catalytic activity were also investigated, with the uniformity of the washcoat being improved by the addition of the dispersant. Additionally, the catalytic activity of the monolithic catalyst was investigated under optimised conditions. This paper covers research conducted on the determination of the powder catalyst formula and the optimization of the monolithic catalyst preparation process in a systematic manner; the results of our work will help to solve the bottleneck problem in the preparation of monolithic catalysts and the practical engineering application of monolithic catalysts.

2. Results and Discussion

2.1. Catalytic Combustion Performance of $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Pd-Ce}/\gamma\text{-Al}_2\text{O}_3$ Powder Catalyst

Firstly, the powder catalyst was investigated in our experiment. From Figure 1a, it can be seen that the activity of the $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst increased with the increasing of the temperature. The higher the Pd content of the catalyst was, the greater the catalytic activity of the catalyst was. However, the T_{10} of each catalyst was higher than 150°C , and the toluene degradation rate of each catalyst was less than 90% at 200°C .

As shown in Figure 1b, the catalytic activity of the catalyst also increased with the increasing of the temperature. With the addition of a small amount of the rare earth element Ce, the catalytic activity of the catalyst increased with the increasing of the Ce content. When the content of CeO_2 was 0.3 wt%, the T_{10} was lower than 150°C , which greatly strengthened the catalytic activity of the catalyst in the low-temperature region (especially $160\text{--}200^\circ\text{C}$). However, the removal efficiency of toluene was more than 90% at 200°C , and it was completely transformed at 220°C . The catalytic efficiency was equivalent to that of 0.7%

Pd/ γ -Al₂O₃ catalyst, due to the synergistic effect between PdO and CeO₂, which promoted the breaking of the Ce-O bond [28], which produced more mobile oxygen and oxygen vacancy and enhanced the catalytic oxidation activity of the catalyst [29]. The activity of the Pd/Ce catalyst began to decrease with the further addition of Ce, but its activity was still higher than that of the 0.2% Pd/ γ -Al₂O₃ catalyst without CeO₂ addition. When the content of CeO₂ increased higher than 3 wt%, the catalytic activity of the catalyst was inhibited, and the catalytic activity of the catalyst for toluene was lower than that of the catalyst without CeO₂. The results showed that the interaction between CeO₂ and PdO was the main factor affecting the surface oxygen vacancy of the catalyst when the addition of CeO₂ was 0.1–2%, which strengthened the catalytic oxidation performance of the catalyst. Based on the above, the 0.2Pd-0.3Ce/ γ -Al₂O₃ catalysts had the best toluene catalytic activity, which was investigated as an active phase of the monolithic catalyst in a continuous experiment. The density of the 0.2Pd-0.3Ce/ γ -Al₂O₃ catalyst was 4.1 ± 0.05 g/cm³.

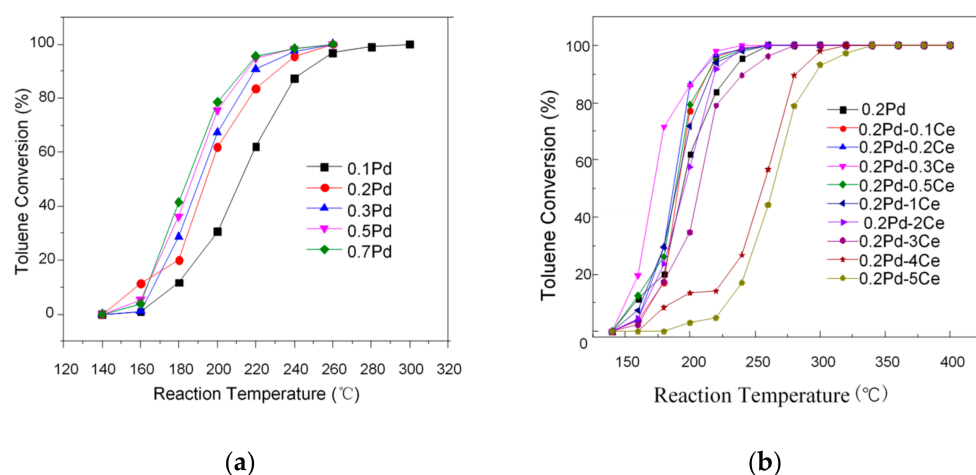


Figure 1. Effects of different Pd contents (a) and Ce contents (b) for toluene catalytic oxidation.

2.2. Catalytic Combustion Performance of the Monolithic Catalyst

As mentioned above, the monolithic catalysts are widely used in practical applications, and the performance of the catalysts' components, such as the substrate and washcoat, would affect the catalytic capabilities. Thus, in our experiment, the effects of the substrate pretreatment and the washcoat on the catalytic capabilities were investigated.

2.2.1. Effect of Substrate Pretreatment on the Performance of the Catalyst

Since the specific surface area of the cordierite substrate is too small (<1 m²/g), it is not conducive to the dispersion of active phase. Acid treatment is often used to improve the specific surface area, thus improving the washcoat upload ratio. In our experiment, three kinds of pretreatment methods were investigated to evaluate the effect on the washcoat upload ratio. At the same time, the effects of different acids on the washcoat upload ratio were discussed. HCl, HNO₃, and citric acid were explored. The experimental results are shown in Figure 2.

From Figure 2, we can see that the effects of acid pretreatment conditions on the washcoat upload ratio were as follows: heating pretreatment > ultrasonic pretreatment > ordinary pretreatment. Using HCl and HNO₃ as the pretreatment acids, the washcoat upload ratio could be improved to different degrees. Both of them had the higher washcoat upload ratios than the citric acid. Besides, HCl had the highest washcoat upload ratio among them. When the substrate was treated with HCl with a concentration of 20%, the washcoat upload ratio could rise up to 17.5%, as shown in Figure 2a. When the HCl concentration was higher than 20%, the washcoat upload ratio was decreased. Compared to untreated cordierite substrate, pretreatment of cordierite substrate with inorganic acid could improve its adsorption capacity. Therefore, pretreatment of the substrate could change its pore

structure. The surface impurities of cordierite were washed away, and the matrix structure and pore channels were fully exposed so that the specific surface area and pore volume were greatly improved, and the washcoat upload ratio was further enhanced.

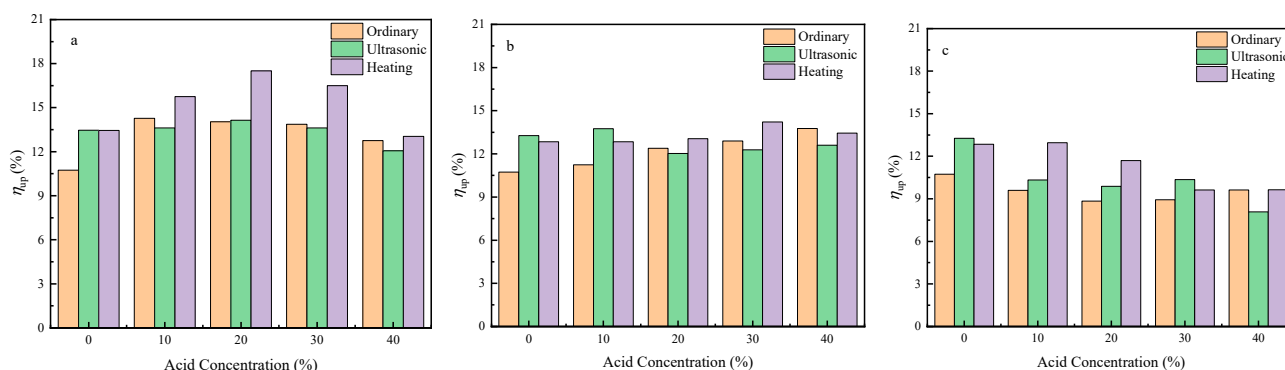


Figure 2. Changes in upload ratio of cordierite under different acid pretreatment conditions. (a) HCl pretreatment, (b) HNO₃ pretreatment, (c) Citric acid pretreatment.

As can be seen from Table 1, Figure 3a,b, the specific surface area of the untreated cordierite substrate was 1.0 m²/g and the pore volume was 1.3 × 10^{−3} mL/g using N₂ sorption. After pretreatment with acid, the pore volume and specific surface area of the substrate increased. For the HCl heating pretreatments, the pore volume and the specific surface area of the substrate could be enhanced effectively. Here, the main reason for the increase in the upload ratio was the increase in pore volume. However, for the heating treatment with 10% and 20% HCl, the specific surface area increased to over 10 m²/g, which was a nearly 10-fold increase compared to without pretreatment, and the pore volume also increased 2–3 times. However, it is impossible to accurately judge whether a substrate material is a macroporous material through the N₂ adsorption–desorption method, so the mercury porosimetry method was used instead in this study. It can be seen from Table 1 that the specific surface area of the substrate pretreated in different ways did not change much, and did not exceed 1 m²/g; however, compared to the untreated substrate, the specific surface area of the substrate material could be improved using inorganic acid treatment. When analysing the porosity of the substrate material, it was found that the particle size distribution was mainly concentrated in the range of 500–5000 nm, which showed that the substrate material is a macroporous material, as shown in Figure 3d. This was also proven using the Hg intrusion/extrusion curves shown in Figure 3c.

Table 1. Changes in specific surface area and pore properties of cordierite substrate before and after pretreatment.

Cordierite Substrate	N ₂ Adsorption		Mercury Porosimetry	
	Surface Area (m ² /g)	Pore Volume (×10 ^{−3} mL/g)	Surface Area (m ² /g)	Pore Volume (mL/g)
Without pretreatment	1.0	1.3	0.571	0.2906
10% HNO ₃ —ordinary	1.7	2.0	0.777	0.3244
20% HCl—ordinary	1.3	1.9	0.648	0.3429
20% HCl—heating	10.1	4.4	0.849	0.3490
10% HCl—heating	10.8	3.9	0.862	0.3436
10% Citric acid—heating	1.2	1.6	0.577	0.3470

Based on the information given above, we can see that acid treatment could increase the specific surface area and pore volume of the cordierite carrier, which could increase the washcoat upload ratio. For the monolithic catalyst substrate, the improvement of pore capacity has two advantages. First, a larger pore capacity can incorporate more

catalyst washcoat and improve the upload ratio of the active phase. Second, a larger pore volume can increase the accumulation of impurities in the catalytic reaction process, thus prolonging the service life of the monolithic catalyst [23].

To investigate the effect of acid treatment on the surface impurities of the cordierite substrate and the surface morphology, the micro-surface morphological characterisation of the cordierite substrate before and after effective 20% HCl treatment was performed. Furthermore, surface EDS analysis provided information on the element, mass percentage, and error, respectively. The results are shown in Figure 4.

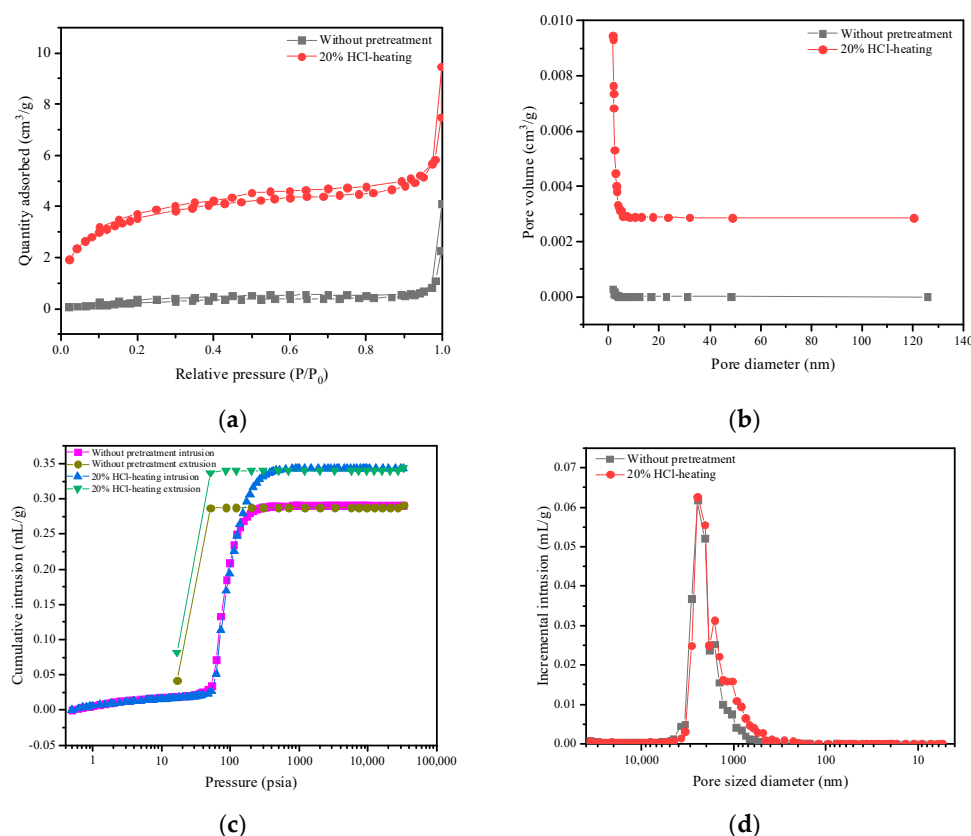


Figure 3. N₂ and mercury sorption isotherms and pore size distributions of cordierite substrate. (a) N₂ sorption isotherms, (b) Pore size distributions (N₂), (c) Mercury intrusion/extrusion curves, (d) Pore size distributions (Hg).

As mentioned above, without acid pretreatment, the specific surface area of the substrate was small. However, the specific surface area and the pore volume of the substrate could increase with acid pretreatment through either the N₂ adsorption–desorption method or the mercury porosimetry method. Furthermore, from Figure 4, it can be seen that the surface chemical composition was not significantly changed with or without acid treatment, and the main elements were O, Si, Al, Mg, and C. On the other hand, this can be explained by the fact that the pretreatment of cordierite with acid solution does not change the chemical properties of cordierite. Furthermore, from the surface morphology, we could not see the obvious changes of the substrate before and after acid treatment.

To verify whether pretreatment of the cordierite with acid would affect the catalytic efficiency of the integral catalyst, the cordierite before and after acid treatment was used as the substrate, 0.2Pd-0.3Ce/ γ -Al₂O₃ catalysts were used as the active phase to prepare the integral catalyst, and its catalytic degradation performance of toluene was evaluated. Cordierites pretreated with 10% HCl heating and 20% HCl heating were chosen as the modified cordierites to evaluate the catalytic activity of toluene. As can be seen in Figure 5, when the cordierite was pretreated, the specific surface area of cordierite and the upload ratio of washcoat increased, so the catalytic activity of the monolithic catalyst increased. The

cordierite pretreated with 20% HCl under heating conditions had the best low-temperature activity. The T_{10} of the toluene catalysis was 142 °C, 10 °C lower than that of the original cordierite. The T_{90} of the toluene catalysis was 200 °C, slightly lower (about 5 °C) than that of the original cordierite. Furthermore, the expansion of the pore volume was conducive to the improvement of the mass of the impurities generated during the catalytic reaction. When the cordierite was pretreated with 10% HCl under heating conditions, the catalytic efficiency was slightly lower than that obtained with the 20% HCl heating treatment.

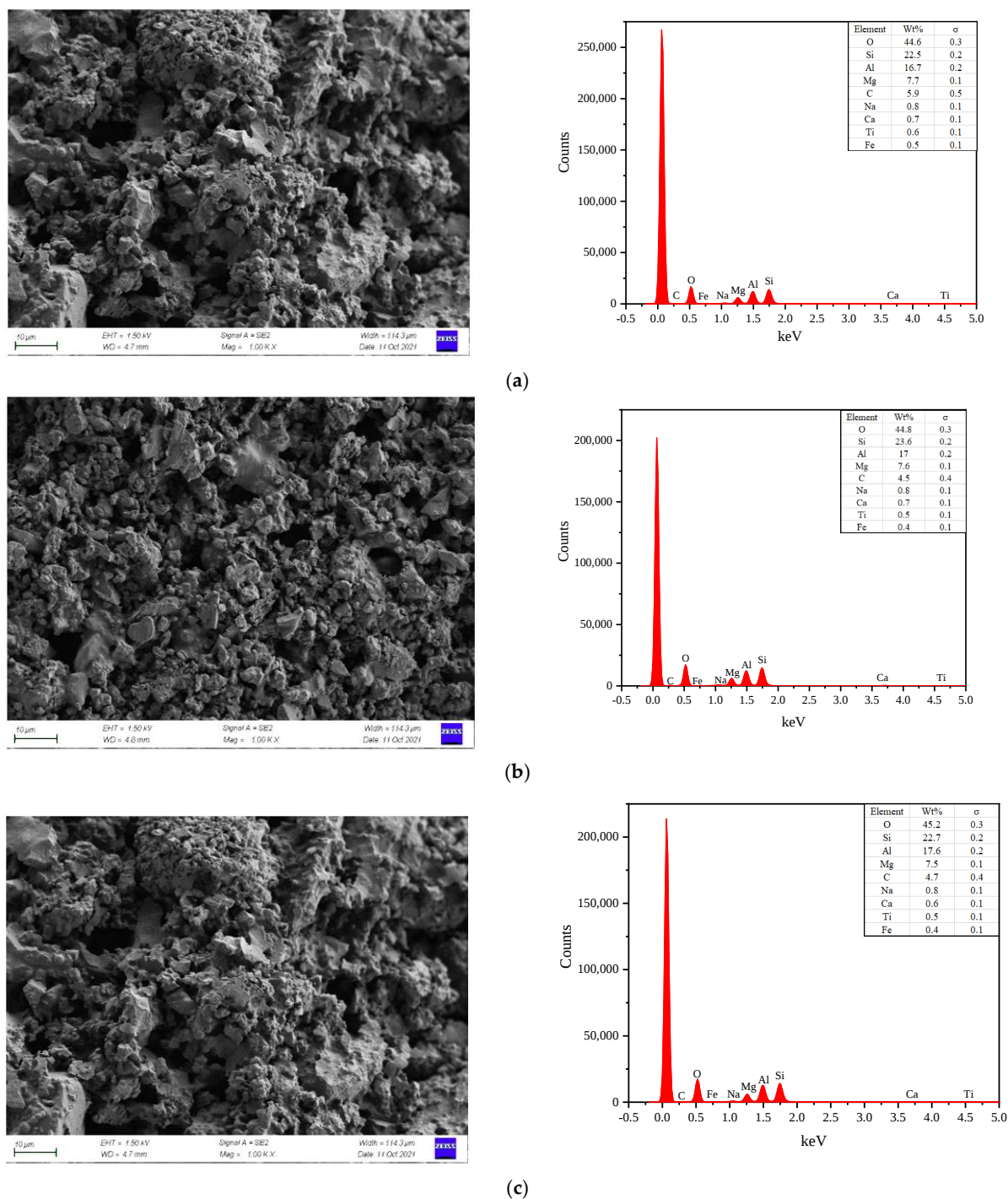


Figure 4. Surface morphology and energy spectrum of cordierite substrate before and after acid treatment ($\times 1000$). (a) Without pretreatment, (b) 20% HCl—Ordinary, (c) 20% HCl—Heating.

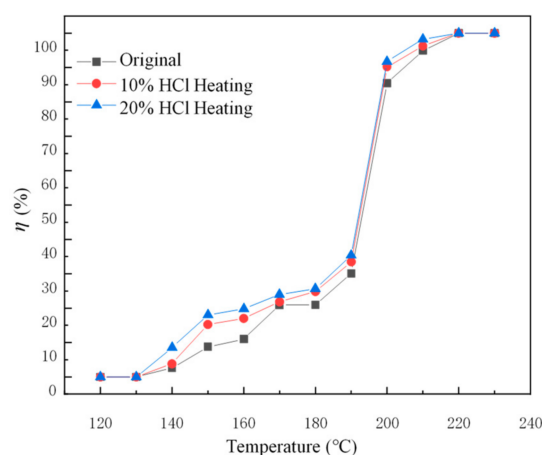


Figure 5. Catalytic activity of toluene for different pretreatments.

2.2.2. Effect of Particle Size of the Washcoat on the Performance of the Catalyst

The particle size of the washcoat affects the catalyst upload ratio. The upload ratio and uniformity can be improved by reducing the particle size [30]. Ball-milling is the most commonly used method to reduce the particle size of a washcoat [31]. In our experiment, the effects of different rotation speeds on the particle size and the upload ratio were investigated.

Figure 6a shows the size of the catalyst washcoat prepared by ball milling (ratio of grinding media to material) for two hours at different rotation speeds. The powder catalyst was screened out through a 20-mesh screen. The particle size of the catalyst could be greatly reduced by ball-milling. When the speed was 300 rpm, the particle size of the catalyst in the washcoat was 3.89 μm . As the rotational speed increased, the particle size decreased further. At a rotation speed of 500 rpm, the particle size reached a minimum of 1.87 μm . At this speed, the ball-milling fragmented the larger catalyst particles, which were further sheared upon interaction with the zirconia pellets. When the rotation speed was further increased to 600 rpm, the particle size did not decrease further but rather increased. This was mainly due to the agglomeration of smaller particles. The main reasons for this phenomenon were mainly due to the surface action of particles, the Brownian movement, and the Van der Waals' forces [32,33].

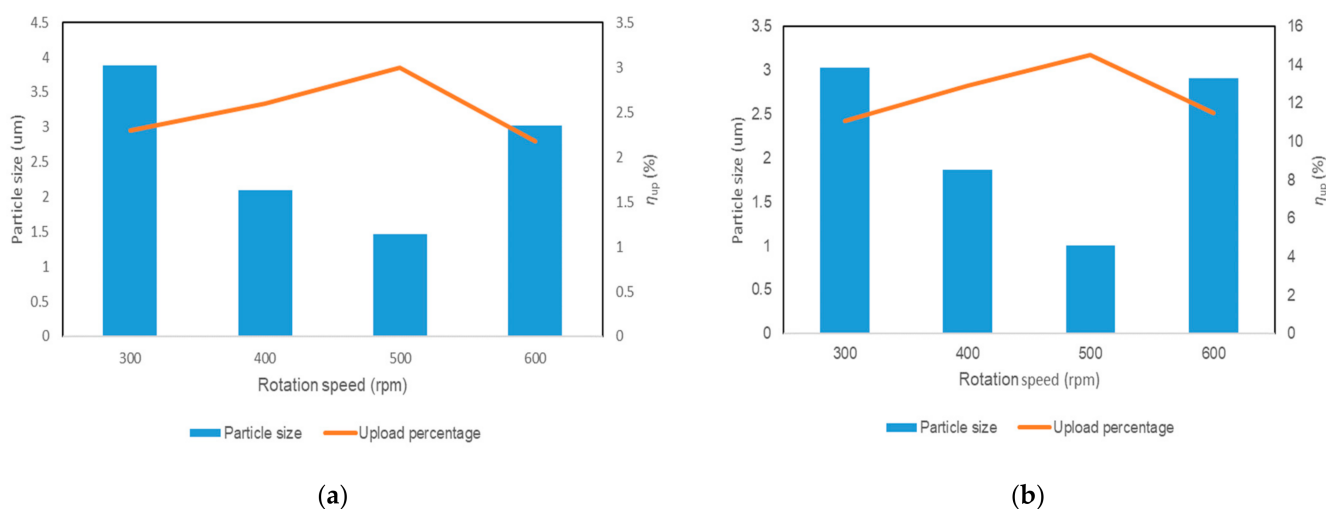


Figure 6. The particle sizes obtained at different rotation speeds and the relationship between the particle size and the upload ratio. (a) Without additives, (b) 25% silica sol.

Figure 6b shows that the size of the washcoat could be further reduced after adding silica sol, reaching the minimum size of 1.01 microns at a rotating speed of 500 rpm. When the particle size was small, the first layer of particles could pile up at the orifices and press closely to their inner walls. Additionally, the smaller particles had a larger adsorption capacity and could, therefore, better adsorb on the surface of the substrate, thereby improving the adhesion of the washcoat. After a layer of small particles was adsorbed on the surface of the substrate, a second layer of particles formed. As the surface formed by small particles was more compact than that formed by large particles, the surface had smaller pores or even no pores, as shown in Figure 7a. At the same time, the smaller the particle size of the washcoat, the better the specific surface area of the whole catalyst, which was advantageous in terms of the catalytic reaction. If the particle size was large, the particles could not accumulate in the interior of the pores but aggregated on top of the pores, as seen in Figure 7b. The washcoat adhesion was low and large holes could readily form on the surface of the washcoat.

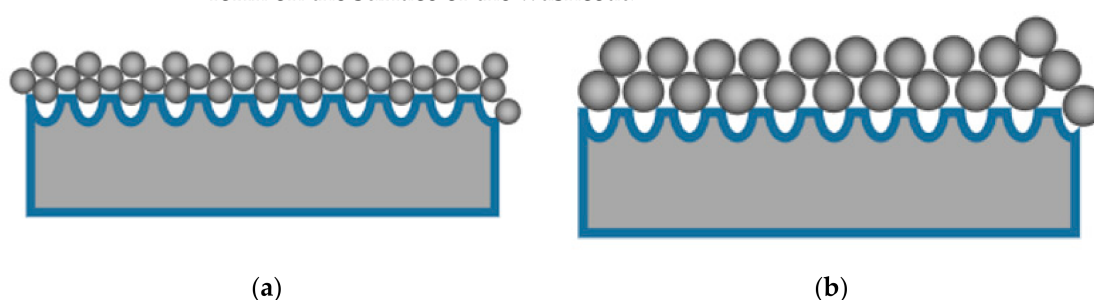


Figure 7. Adsorption model of different particle sizes on the cordierite substrate surface. (a) 1.01 μm , (b) 2.91 μm .

The results of the catalytic performance of the monolithic catalysts prepared with different washcoats are shown in Figure 8. The conditions were as follows: the active phase was 0.2Pd-0.3Ce/ γ -Al₂O₃; the substrate was cordierite; the particle sizes of the washcoat were 3.03 μm , 1.87 μm , 1.01 μm and 2.91 μm , respectively; 25% silica sol was used as additives. As discussed above, particle size had a considerable influence on the surface morphology of the monolithic catalysts. Small particle size was conducive to the distribution of active phase on the substrate surface, which decreased the agglomeration of active phase and increased the number of active centres, thereby improving the catalytic activity. The catalytic degradation toluene improved as the washcoat size decreased. When the particle size of the catalyst washcoat was 1.01 μm , the T₁₀ and T₉₀ values were about 10 °C lower than those of the monolithic catalyst prepared from the 3.03 μm catalyst washcoat. Additionally, the high-temperature performance of the monolithic catalyst prepared from catalyst washcoat with dispersant was better than without dispersant; there was no significant difference in its activity at low temperature.

2.2.3. Effect of Dispersant on the Performance of the Catalyst

The dispersion of the catalyst washcoat affects the uniformity of the monolithic catalyst in the process of preparing the monolithic catalyst. In the present study, the effects of stirring dispersion alone and stirring + ultrasonic dispersion on dispersion properties were studied. Polyacrylic acid (PAA) and polyvinyl pyrrolidone (PVP) were selected as dispersants. The stirring speed and ultrasonic power were 500 rpm and 40 kHz, respectively.

The Zeta potential of different catalyst washcoat was measured, while this method is usually a measure of the strength of the repulsive or attractive force between particles [34]. The smaller the molecules or dispersed particles, the higher the absolute value of the zeta potential and the more stable the system [35].

Figure 9 shows the variation in the zeta potential as a function of the type and concentration of the dispersant, in which PAA-stir means PAA with stirring, PAA-ul + stir means PAA with ultrasonic and stirring, PVP-stir means PVP with stirring, PVP-ul + stir means

PVP with ultrasonic and stirring. In Figure 9, it can be seen that when the stirring time was the same, the dispersion properties of the suspensions obtained with the inclusion of ultrasonication were better than for the suspensions obtained by stirring alone. PAA provided a better dispersion performance than PVP, which was consistent with the phenomenon observed in the literature [36]. The stability of the suspension was optimal when the PAA concentration was 4%, for which the Zeta potential was -30 mV. As the PAA concentration increased to 4%, the adsorption of PAA on the surface of the Al_2O_3 particles increased, the electrostatic repulsion between particles increased, the settling volume of the suspension decreased, and the stability increased. When the concentration of PAA was 4%, the absolute value of the zeta potential reached a maximum, the suspension stability was optimal, and the adsorption of PAA on the surface of the Al_2O_3 particles reached saturation. When the concentration of PAA was further increased, the amount of free PAA in the solution increased; this produced a bridging effect, resulting in a decrease in the Zeta potential and a slight deterioration of the suspension stability.

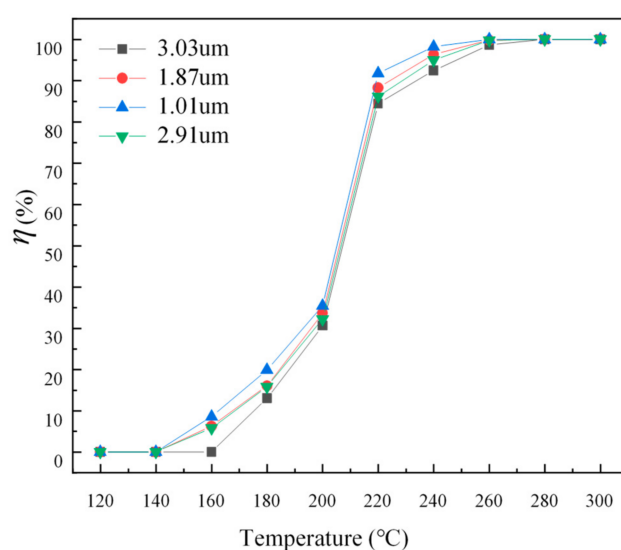


Figure 8. Effect of the particle size of the washcoat on the toluene catalytic activity.

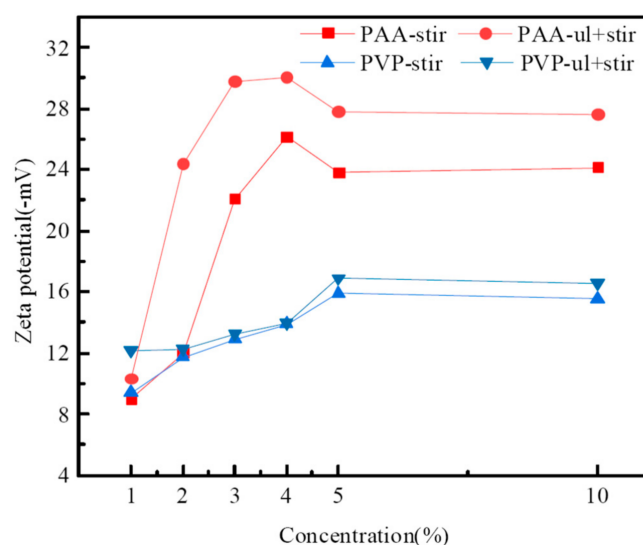


Figure 9. Zeta potential of washcoat with different dispersion properties.

Figure 10 shows the SEM results of different washcoats. In Figure 10c, it can be seen that PAA could enhance the stability of the washcoat. Many cracks and holes can be seen in

Figure 10a,b; these would have led to the decrease in the catalytic performance. Based on the above, PAA had a better dispersion performance, which was consistent with the results of the SEM tests.

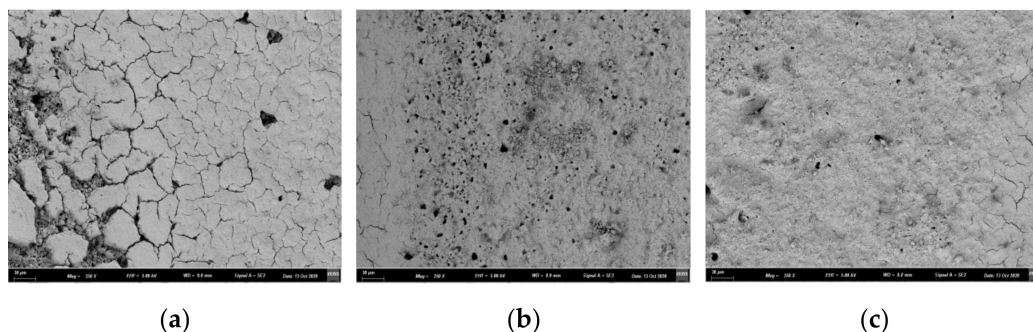


Figure 10. Surface morphology of washcoat ($\times 250$). (a) without dispersant, (b) 4% PVP, (c) 4% PAA.

In order to further explore the influence of the dispersant on the performance of the monolithic catalyst, the effect of the dispersant on the catalytic capabilities was investigated in our experiment, as shown in Figure 11. The conditions were as follows: the active phase was 0.2Pd-0.3Ce/ γ -Al₂O₃; the substrate was cordierite; the particle sizes of the washcoat was 1.01 μ m; 25% silica sol was used as additives; PVP and PAA was used as the dispersant.

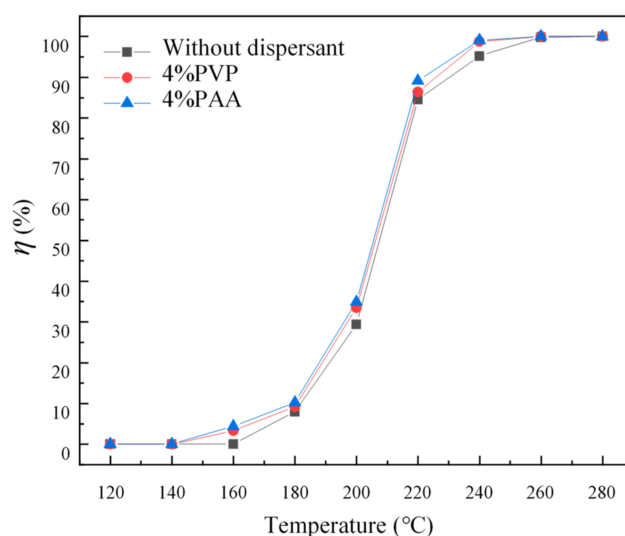


Figure 11. Catalytic degradation of toluene with the monolith catalysts.

It can be seen in Figure 11 that the monolithic catalyst prepared from three different types of dispersant had little effect on the degradation efficiency of toluene. The T_{10} of the three monolithic catalysts was almost the same, but the T_{90} of the monolithic catalyst prepared with 4% PAA was about 10 °C lower than that prepared without dispersant. At the same time, when PAA was used as a dispersant, the efficiency of monolithic catalyst was slightly better than that of PVP, which was consistent with the results of the Zeta potential. In general, the dispersion treatment of the washcoat was conducive to the improvement of the catalytic capabilities of the monolithic catalyst.

2.2.4. Catalytic Degradation of Toluene with the Optimized Catalyst

Based on the discussions above, we investigated the effects of the substrate pretreatment, the particle size of the washcoat, and the dispersant on the performance of the catalysts. The optimized preparation conditions of monolithic catalyst were determined, namely, a pretreatment method of 20% HCl heating, a particle size of the washcoat of

1.01 μm , and the dispersant of PAA benefitting from the removal of toluene. Thus, the catalytic degradation of toluene with the optimized catalyst was evaluated in our experiment, as shown in Figure 12. The conditions were as follows: the active phase was 0.2Pd-0.3Ce/ γ - Al_2O_3 ; the substrate was 20% HCl heating of cordierite; the particle sizes of the washcoat was 1.01 μm ; 25% silica sol was used as additives; PAA was used as the dispersant.

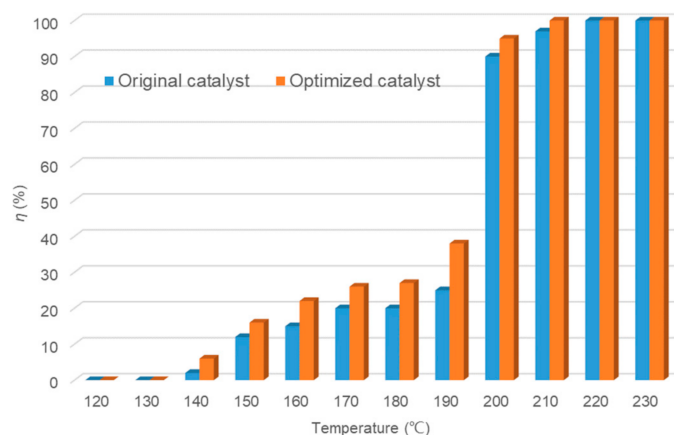


Figure 12. Catalytic degradation of toluene with the optimized catalyst.

From Figure 12, we can see that the optimized catalyst had better catalytic performance than the original catalyst. The T10 and T90 of the optimized catalyst were about 5 °C lower than that of the original catalyst. For the optimized catalyst, the catalytic oxidation efficiency could be attained 100% at 205 °C, almost the same as the powder catalyst.

3. Materials and Methodology

3.1. Materials

As the substrate, 300 meshes of cordierite honeycomb ceramics ($\varnothing$ 20 mm $\times$ 15 mm, Jinrui, Yixing, China) were chosen. Analytical-grade HCl, HNO_3 , and citric acid were used as pretreatment agents (Sinopharm, Beijing, China). Silica sol (AR), PAA (polyacrylic acid, AR) and PVP (polyvinyl pyrrolidone, AR) were used as the raw materials of monolithic catalysts (Honghu, Beijing, China). γ - Al_2O_3 was selected as the washcoat (Lianlian, Lianyungang, China).

3.2. Experiment and Apparatus

(1) Preparation of the Pd/ γ - Al_2O_3 & Pd-Ce/ γ - Al_2O_3 catalyst

The catalyst was prepared by equal volume impregnation method: the 0.1 mol/L H_2PdCl_4 solution (1.67 mL) and 40 mL deionized water were stirred ultrasonically at 60 °C for 1 h. After the solution was completely mixed, 9.9 g γ - Al_2O_3 powder was added slowly and ultrasonic stirring was continued for 3 h. Then, 0.1% Pd/ γ - Al_2O_3 catalyst (mass fraction, the same as below) was prepared by drying at 110 °C for 4 h, before being calcined at 550 °C for 3 h, and was then ground and sifted to 20 to 40 mesh for use. Other x% Pd/ γ - Al_2O_3 catalysts (x = 0.2, 0.3, 0.5, 0.7) were prepared according to the stoichiometric ratio described above.

The 0.2% Pd-0.3% Ce/ γ - Al_2O_3 catalysts were prepared from 0.1 mol/L H_2PdCl_4 solution 3.33 mL and 0.1 mol/L $\text{Ce}(\text{NO}_3)_3$ 1.94 mL according to the above method, ground and sifted to 20 to 40 mesh for use. Other 0.2% Pd-x% Ce/ γ - Al_2O_3 catalysts (x = 0.1, 0.2, 0.5, 1, 2, 3, 4, 5) were prepared by means of the stoichiometric ratio according to the above method.

(2) Substrate pretreatment

The cordierite honeycomb ceramic was washed with deionised water and dried at 110 °C for 2 h. The performance of pretreatments with different types of acid was compared

to the untreated substrate. Substrate samples were treated with different concentrations of HCl, HNO₃, and citric acid under different conditions for 3 h, then rinsed with deionised water until the pH was 7. The pretreatment methods were: (I) ordinary treatment at room temperature; (II) ultrasonic pretreatment at 40 kHz; (III) heating in a 70 °C water bath. The samples were then dried at 110 °C for 2 h and calcined at 550 °C for 3 h. The heating temperature was 70 °C in the water bath.

(3) Preparation of the catalyst washcoat

The chosen active phase, 0.2. Pd-0.3Ce/ γ -Al₂O₃, was mixed with alkaline silica sol and deionized water in proportions of 0.1:0.25:0.61, respectively (mass fraction). The mixture was ball-milled for 2 h at a rotational speed of 500 rpm, then 4% of PAA dispersant was added and the washcoat was stirred for 30 min under ultrasonication.

(4) Preparation of monolithic catalyst

The monolithic catalyst was prepared by the general impregnation method. The pretreated substrate was impregnated in washcoat for 3 h, dried at 110 °C for 4 h, and calcined at 550 °C for 3 h. The monolithic catalyst without substrate pretreatment was prepared by the same method. The workflow is shown in Figure 13.

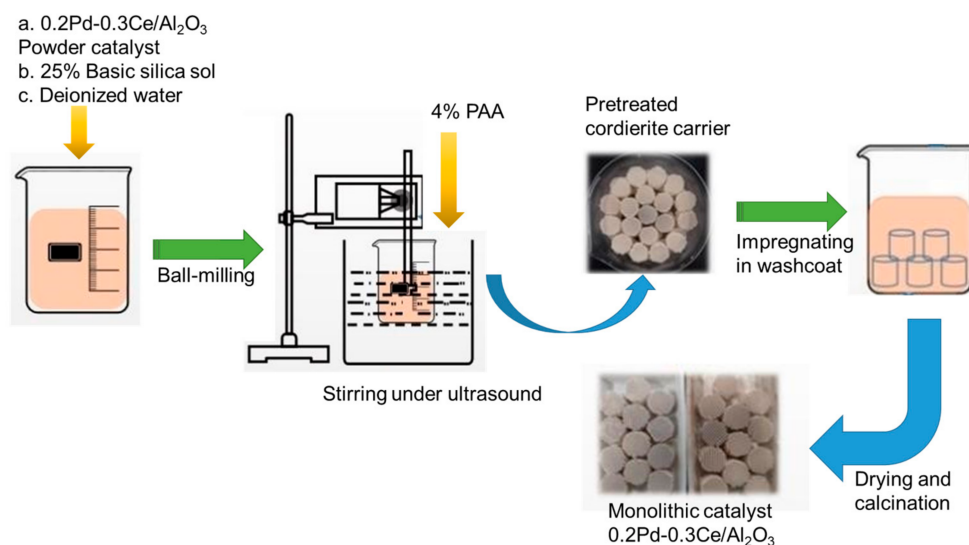


Figure 13. Process of preparation of monolithic catalyst.

(5) Catalytic properties characterization

The sample was pretreated at 100 °C for 1 h before the test. The test sample was approximately $2 \times 2 \times 4 \text{ mm}^3$ of granular mass. The specific surface area and pore structure of the catalyst were analysed using an automatic adsorption instrument (Gemini V, Micromeritics, Atlanta, GA, USA) and calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The adsorption and desorption curves were tested using a low-temperature N₂ physical adsorption method with high-purity N₂ (purity >99.99%). The pore sizes of the cordierite substrate were also analysed using the mercury (Hg) intrusion porosimetry performed on an automatic analyser (AutoPore IV 9500, Micromeritics, Atlanta, GA, USA). The surface morphology of the substrate and monolithic catalyst was observed and analysed with a SEM (Gemini SEM 300, Carl Zeiss AG, Oberkochen, Germany). The flaky test sample was $4 \times 4 \text{ mm}^2$. A potentiometer was used to test the Zeta potential of the catalyst slurry and the dispersion property of the catalyst slurry with different contents of the dispersant (Malvern ZSE, Malvern, UK). Particle size analyzer (NICOMP 380, PSS, Santa Barbara, CA, USA) was used to test the particle size of the washcoat.

The monolithic catalyst upload ratio refers to the ratio between the catalyst washcoat loading and the initial mass of the sample before and after coating. The upload ratio was calculated according to Equation (1)

$$\eta_{\text{up}} = \frac{M_1 - M_0}{M_0} \times 100\% \quad (1)$$

where η_{up} is the monolithic catalyst upload ratio, %; M_1 is the sample mass after calcination, g; M_0 is the initial mass of the sample, g.

All of the samples were prepared in triplicate. After data measurements were obtained, the mean value was taken, and the standard error was calculated.

(6) Catalyst evaluation

The toluene catalytic activity of the catalyst was evaluated by a self-made atmospheric pressure fixed-bed reactor (inner diameter of 18 mm, constant temperature zone length of 80 mm). The experimental conditions were as follows: the 4 mL catalyst was put into the constant temperature zone of the reactor without any pretreatment, the catalyst bed was about 15 to 16 mm high, the thermocouple was placed in the upper part of the catalyst bed, and the temperature of the reactor was controlled by temperature controller. The heating rate was 5 °C/min. Under normal pressure, toluene saturated steam was produced by blowing toluene generating bottle with clean air as a carrier gas (O_2 content of 21%, N_2 content of 79%), toluene waste gas with toluene concentration of 3000 mg/m³ was obtained, and the total flow rate of 2 L/min flowed through the catalyst bed. The space velocity was 30,000 h⁻¹. The concentrations of toluene at the outlet and inlet of the reactor were determined by Agilent GC7890 gas chromatography. The temperatures corresponding to the catalytic efficiency of 10%, 50% and 90% of toluene were represented by T_{10} , T_{50} and T_{90} , respectively, and the catalytic efficiency of the catalyst was expressed by Equation (2).

$$\eta = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \quad (2)$$

where η represents the catalyst catalytic efficiency (%), C_{in} represents the reactor inlet gas toluene concentration (mg/m³), C_{out} represents the reactor outlet gas toluene concentration (mg/m³).

4. Conclusions

In the present work, the research on the determination of powder catalyst formula and the optimization of monolithic catalyst preparation process was carried out systematically.

- (1) The activity of the Pd/ γ -Al₂O₃ catalyst increased with the increasing of the temperature. With the addition of a small amount of the rare earth element Ce, the catalytic activity of the catalyst increased with the increasing of the Ce content. It was found that the 0.2Pd-0.3Ce/ γ -Al₂O₃ catalysts had the best toluene catalytic activity.
- (2) The pretreatment of the cordierite with 20% HCl could improve the properties of the cordierite. When the cordierite was pretreated, the monolithic catalytic activity of the catalyst increased. Cordierite pretreated by 20% HCl under heating conditions had better low-temperature activity.
- (3) The upload ratio was inversely proportional to the size of the washcoat. Reducing the size of the catalyst particle in the washcoat could increase the loading ratio and the specific surface area. When the particle size of the washcoat decreased from 3.03 micron to 1.01 micron, the loading ratio increased by nearly 3%. At the same time, the T_{10} and T_{90} of the catalytic degradation of toluene were reduced by about 10 °C. It was observed that 4% PAA had the best dispersion performance for the washcoat. The catalytic efficiency of the monolithic catalyst increased as a result of the substrate pretreatment, adjusting the washcoat particle size, and improving the washcoat dispersion property.

For future research, it is necessary to carry out more systematic research about the additive types and the substrate properties of the monolithic catalyst, and to conduct performance tests in relation to its practical applications.

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