Effect of the Properties of Cordierite Support and Catalyst Slurry on the Catalytic Degradation of Toluene by Monolith Catalyst

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Abstract

Monolithic catalysts are widely used in industrial catalysis. However, in the preparation of monolithic catalyst, the most important catalyst coating has the problems of low upload rate and poor uniformity. In the present work, the effects of acid treatment of carrier on the upload rate and the effects of size of slurry and dispersant on the uniformity of coating were investigated. The weight loss rate and water absorption rate of cordierite, slurry stability, coating upload rate and catalytic performance were also tested. Characterization analysis was carried out by means of BET, SEM, Zeta potential, the laser grain-size analyzer. The results showed that the optimal performance of cordierite carrier could be obtained by heating the cordierite carrier with 20% HCl for 3 h; the water absorption rate could increase for more than 48.0%, and the upload rate could reach 14.5%. Pearson test showed that there was a moderate positive correlation between water absorption rate and upload rate. It was also found that reducing the particle size of the slurry (1.47 microns) and adding 4% dispersant PAA could effectively improve the stability of the suspension and the uniformity of the coating. When 20% HCl was used to pretreat, the toluene catalytic activity of the monolith catalyst prepared by cordierite increased, in which T_{10} and T_{90} both increased for about 5 °C. At the same time, reducing particle size and adding dispersant could also promote the catalytic degradation efficiency to a certain extent.

1. Introduction

The rapid development of industry has complicated the types of VOCs emitted^[1]. In the current VOCs removal process, catalytic combustion is one of the more mature and widely used technologies, which transforms VOCs into pollution-free substances at low temperature through the action of catalyst^[2]. In practical industrial applications, monolithic catalysts are widely used because of their lower bed pressure^[3], better interphase mass transfer^[4] and heat transfer performance^[5] compared with powder catalysts. At present, honeycomb ceramics is commonly used as the carrier of integral catalyst, which has the advantages of regular shape and high mechanical strength^[6].

As one of the commonly used carriers for monolithic catalysts, cordierite ceramics has excellent mechanical strength and thermal expansion coefficient, but it also has 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 to a low catalyst loading rate^[7–9]. In the application of monolithic catalysts, the upload rate is an important factor affecting the activity of monolithic catalysts^[10], and monolithic catalysts with a high upload rate will have a high reaction activity. In order to obtain a larger specific surface area, the commonly used methods include: 1. Prepare carrier coating by loading a carrier with a high specific surface area on the surface of the carrier^[11–14]; 2. The cordierite surface was treated with acid treatment^[15–17]. At present, alumina, titanium dioxide, molecular sieve is used more coating materials. Lai et al.^[18] used alumina as the coating carrier to prepare $\text{MnO}_x/\text{La-Al}_2\text{O}_3$ monolithic catalyst by incipient wetness impregnation method, the T_{90} of catalytic degradation of toluene was 275°C. Yang et al.^[19] used OMS-2 as the coating carrier to prepare $\text{Co}_3\text{O}_4/\text{OMS-2}$ monolithic catalyst, the contact area of

the catalyst with the same mass can be increased by about 4 times compared with the traditional powder-type catalyst. Lu^[20] and Sun^[21] used different concentrations of nitric acid for acidic pretreatment of the carrier, which not only improved the specific surface area of the carrier, but also increased the loading rate of the coating, thus improving the catalytic performance of the monolayer catalyst. Therefore, the performance of the monolithic catalyst obtained by acid pretreatment of the carrier is better than that obtained by adjusting the proportion of slurry. As we all know, the performance of water absorption and loading of cordierite was important to the catalytic abilities of the catalysts. But relatively few studies have been conducted on the water absorption and load performance of cordierite under pretreatment conditions^[22]. Furthermore, carrier pretreatment is closely related to the active component upload and the service life of the monolithic catalyst^[23], but there are few reports on the carrier treatment system^[24].

At the same time, it is a great significance to study the preparation method of monolithic catalyst coating. A uniform coating plays an important role in the catalytic reaction. And the stability of the slurry is important to obtain a uniform coating^[25]. To obtain a stable slurry, the particles in the slurry needed to disperse effectively. This dispersion depends on the net charge on the surface of the particle^[26]. The exploration of treatment conditions was less in the present research.

The current prepared monolithic catalyst has some problems such as uneven coating and easy to fall off, which reduces the catalytic efficiency of monolithic catalyst. In view of this, it is necessary to systematically study the pretreatment of the monolithic catalyst carrier and the dispersion performance of the catalyst slurry, so as to prepare the monolith catalyst with uniform coating and high catalytic efficiency.

In this study, the treatment effect of different types of acids on the surface of cordierite carrier under different technological conditions was explored, the pretreatment process was optimized and screened to improve the water absorption rate and specific surface area of cordierite carrier, so as to improve the performance of cordierite carrier. At the same time, the influence of ball milling conditions on the size of slurry and the effects of particle size on the loading rate and catalytic activity were also investigated, and the uniformity of coating and the stability of the catalyst slurry was improved by adding dispersant and the best dispersant was screened out. Then the catalytic activities of the monolithic catalyst were investigated under the best conditions.

2. Materials And Methodology

2.1 Materials

300 mesh of cordierite honeycomb ceramics (Ø 20 mm x 15 mm, Yixing, Jiang Su) was chosen as the cylinder sample. HCl, HNO₃, citric acid were analytical reagent and used as pretreatment agentia. Silica sol (AR), PAA (polyacrylic acid, AR) and PVP (polyvinyl pyrrolidone, AR) were used as the raw materials of monolithic catalyst. TiO₂ was selected as the catalyst carrier.

2.2 Experiment and Apparatus

(1). Carrier pretreatment

Cordierite honeycomb ceramics was washed into deionized water, dried at 110 °C for 2 h. The pretreatment performance of different kinds of acid was compared to the untreated carrier. Carrier samples were treated with different concentrations of HCl, HNO₃ and citric acid under different conditions for 3 h, then rinsed with deionized water when pH was 7, dried at 110 °C for 2 h, and roasted at 550 °C for 3 h. The pretreatment was carried out in the following three methods: ① ordinary treatment at room temperature; ② ultrasonic pretreatment at 40 KHz; ③ heating in 70 °C water bath.

(2). Preparation of catalyst slurry

The powder catalyst were prepared by incipient impregnation^[27]: a solution of 3.33 mL of 0.1 mol/L H₂PdCl₄, 1.94 mL of 0.1 mol/L Ce(NO₃)₃ and 38 mL deionized water were stirred using an ultrasonic stirrer at 60 °C for 1 h. After the solution was completely mixed, 9.99 g of TiO₂ powder was added slowly, and stirred for 3 h under the conditions of ultrasonic. The 0.2Pd-0.3Ce/TiO₂ powder catalyst (mass fraction, the same as below) was prepared and dried at 110 °C for 4 h, then was calcined at 550 °C for 3 h.

Slurry preparation: the catalyst powder was mixed with alkaline silica sol and deionized water in a proportion of 0.1:0.25:0.61 (mass fraction), and the catalyst slurry was prepared with ball grinding for 2 h at the rotational speed being of 500 r/min, then 4% dispersant PAA (polyacrylic acid) was added to the slurry and stirred for 30 min under ultrasonic conditions.

(3). Preparation of monolithic catalyst

The monolithic catalyst was prepared by general impregnation method. The pretreated cylinder sample was impregnated in the slurry for 3 h, then the residual slurry was blown out of the pore passage, dried at 110 °C for 4 h, and roasted at 550 °C for 3 h. According to the above method, the monolithic catalyst without carrier pretreatment was prepared simultaneously, and the slurry group was divided into the monolithic catalyst with 20%, 25% acid silica sol and 20% basic silica sol. The specific workflow was shown in Fig.1.

(4). Catalytic properties and characterization

The water absorption, BET, SEM and XRF of cordierite carrier were compared before and after the acid pretreatment, and the upload rate of active components and toluene catalytic activity of cordierite carrier were compared. Meanwhile, the effects of different content and different types of inorganic binder on coating upload rate, expulsion rate, BET and SEM were compared. At the same time, the dispersion of slurry was characterized by Zeta potential and slurry sedimentation tests.

The specific surface area and pore structure of the catalyst were analyzed by a Gemini V (Micromeritics) automatic adsorption instrument and calculated by the Brunauere-Emmete-Teller (BET) and Barrette-Joynere-Halenda (BJH) methods. Adsorption and desorption curves were tested by a low temperature N₂ physical adsorption method with high-purity N₂ (purity >99.99%) as a power source. The sample was pretreated at 100°C for 1 h before the test. The test sample was approximately 2x2x4 mm³ of granular mass.

The surface morphology of carrier and the monolithic catalyst was observed and analyzed with Gemini SEM 300 (Carl Zeiss AG). Metal spraying was 90s and test voltage was 50kV. The flaky test sample was a 4x4 mm².

Malvern ZSE was used to test the Zeta potential of the catalyst slurry and the dispersion property of the catalyst slurry with different content of dispersant. The preheated time was 60 seconds, and the number of cycle tests was 30 times.

NICOMP™ 380 was used to test the particle size of the slurry.

The cylinder cordierite samples before and after treatment were placed in deionized water for 1 h. After the water on the inner and outer surfaces of the channel was blown away, the weight increasing percentage of the sample was the water absorption rate of cordierite. The calculation formula is as follows:

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

Where η_{ab} is the water absorption, %; M_1 is the sample quality after absorption, g; M_0 is the initial mass of the sample, g.

The monolithic catalyst upload rate refers to the ratio between the catalyst slurry loading and the initial mass of the sample before and after coating. The calculation formula is as follows:

$$\eta_{up} = \frac{M_2 - M_0}{M_0} \times 100\% \quad (2)$$

Where η_{up} is monolithic catalyst upload rate, %; M_2 is the sample quality after calcine, g; M_0 is the initial mass of the sample, g.

3 samples were prepared in parallel with all the above samples. After measuring the data, the mean value was taken, and the standard error was calculated. The error range was within 2%.

Evaluation of the activity of the monolithic catalyst: the catalytic activity of toluene was tested in a self-

made fixed bed reactor. The toluene concentration at the reactor inlet was 3000 mg/m³, and the GHSV was 30000h⁻¹. The toluene concentration at the reactor outlet was determined by gas chromatograph (Agilent 7890), and the toluene removal rate was calculated by the following formula:

$$\eta_{re} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (3)$$

Where: η_{re} is toluene removal rate, %; C_{in} is the inlet toluene concentration, mg/m³; C_{out} is the outlet toluene concentration, mg/m³.

3. Results And Discussion

3.1 Effect of carrier pretreatment on the performance of the catalysts

Since the surface of cordierite carrier itself is relatively smooth and the specific surface area is small (<1 m²/g)^[28], it is not conducive to the dispersion of the active components on the surface of the carrier. However, the surface morphology and pore structure can be improved by acid treatment, which benefits to the uniform dispersion of the active components.

(1). Carrier water absorption

After acid treatment of cordierite carrier, the water absorption of cordierite could be greatly improved no matter which pretreatment method was adopted.

In Fig.2, through the heating pretreatment, we can see that the highest water absorption was increase by 48.5%, 46.4% and 48.0% when the acid treatment was 20% HCl, 10% HNO₃ and 20% citric acid, respectively. Through the ultrasonic pretreatment, the highest water absorption was increase by 48.9%, 43.4% and 35.7% when the acid treatment was 10% HCl, 20% HNO₃ and 40% citric acid, respectively. While through the ordinary pretreatment, the highest water absorption was increase by 66.2%, 67.2% and 57.5% when the acid treatment was 10% HCl, 10% HNO₃ and 10% citric acid, respectively. Without pretreatment, the hydrophobic impurities on the carrier surface, restricted the water absorption of the carrier, so the water absorption rate is the lowest. Through ordinary processing, the surface hydrophobic material can be washed off, makes the water absorption rate increase. The reason is that ordinary processing could completely remove surface impurities, which benefitted to the water absorption rate highest. The water absorption rate comes from two facts:(1) the water absorption of the carrier; (2) Water absorption of impurities on the carrier surface. In addition, from the change analysis of weight loss rate and subsequent SEM test results, the cordierite after ordinary treatment has the lowest weight loss rate (As shown in Fig.1), and its relatively rough surface can also indicate that ordinary treatment has a poor removal effect on surface impurities. The surface impurities were thoroughly removed by ultrasonic treatment and heating treatment. In this case, the water absorption rate of cordierite basically due to the water absorption of the carrier itself, which could further prove the water absorption performance of the

carrier itself. So in our experiment, the water absorption rates of 20% HCl, 20% citric acid with heating treatment and 10% HCl with ultrasonic treatment were higher than 35.0%, the highest water absorption rate could reach 36.8%.

(2). Coating upload rate

With HCl and HNO_3 being used as pretreatment acids, the upload rate was improved to different degrees under three treatment conditions. The overall upload rate was up to 12-14%. The pretreatment conditions with the upload rate larger than 14.0% were 10% HCl ordinary treatment, 10% HCl heating treatment and 20% HCl heating treatment, and 30% HNO_3 heating treatment respectively, and the upload rates were 14.4%, 14.3%, 14.5% (the highest) and 14.2%, respectively. By acid treatment, the water absorption and specific surface area could be improved, water absorption rate, specific surface area and pore volume of cordierite carrier increased, which could promote the loading of catalyst slurry, and then increased the loading rate. So in our experiment, the water absorption rate, specific surface area and pore volume were selected as the assessment indexes of the carrier. When citric acid was used as pretreatment acid, the upload rate showed a decreasing trend under the three treatment conditions. High upload rate is more conducive to the use effect of the monolithic catalyst^[29]. In Wang's study^[30], the effect of organic acid as a pretreatment acid is not ideal. Therefore, citric acid is not an ideal pretreatment acid in terms of upload rate alone.

(3). Correlation analysis of water absorption rate and upload rate of carrier

In order to further explain the correlation among the water absorption rate and upload rate of cordierite pretreated with acid solution, the SPSS data analysis software was used for correlation analysis of 36 groups of data. K-S test^[31] can determine whether a set of data belongs to normal distribution, and only the data belonging to normal distribution can be carried out Pearson test. As shown in Table 1, K-S test results showed that the progressive significance (bilateral) of water absorption rate and upload rate was all greater than 0.05, so the two groups of data all conform to the normal distribution, and Pearson correlation test can be performed.

From table 2, the Pearson correlation coefficient between water absorption rate and upload rate was 0.55 > 0, in [0.4, 0.6) interval, water absorption rate and upload rate can be thought of two variables are moderately correlation, and the positive correlation. L Baharudin^[19] also verified this conclusion.

Table 1 K-S test between weight loss rate, water absorption and upload rate of single sample

	N	Normal parameter		Most extreme difference			K-S Z	Asymptotically significant phase (bilateral)
		Mean	Std	Abs	+	-		
water absorption rate		34.51	1.24	0.09	0.09	-0.06	0.52	0.95
upload rate		12.05	1.82	0.13	0.11	-0.13	0.79	0.57
Conclusion: The test distribution is normal distribution.								

Table 2 Pearson test between weight loss rate, water absorption rate and upload rate

	weight loss rate		water absorption rate		upload rate	
	N=36					
	Pearson correlation	Significance (bilateral)	Pearson correlation	Significance (bilateral)	Pearson correlation	Significance (bilateral)
water absorption rate	0.37	0.03	1		0.55	0.00
upload rate	0.19	0.27	0.55	0.00	1	
Conclusion:a.Water absorption and upload rate were significantly correlated at 0.01 level (bilateral).						

(4). BET and SEM

Since the specific surface area of cordierite carrier is small ($<1.0\text{m}^2/\text{g}$), acid treatment is often used to improve the specific surface area frequently, thus improving the slurry upload rate. As can be seen from Table 3, the specific surface area of the untreated cordierite carrier was $1.0\text{m}^2/\text{g}$, and the pore volume was $1.6\times 10^{-3}\text{cm}^3/\text{g}$, both of which were small. After the ordinary treatment with 10% HNO_3 and 20% HCl , both of the pore volume and specific surface area were increased. Meanwhile, as shown in Fig.3, the upload rate were only 13.2% and 11.2%. In this point, the main reason for the increase of upload rate is due to the increase of pore volume. However, the heating treatment with 10% and 20% HCl , the specific surface area was increased to over $10\text{m}^2/\text{g}$, which was increased by nearly 10 times and the pore volume was also increased by 2~3 times than without pretreatment. Meanwhile, as shown in Fig.3, the upload rate had raised to 14.3% and 14.5% respectively. After the treatment with HCl , 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 slurry upload rate was

further enhanced. For the citric acid pretreatment process with low upload rate, the specific surface area of the cordierite changed little, the pore volume and pore size decreased, which led to a low upload rate about 10.0%. According to IUPAC's classification of pore size, the carrier material of cordierite investigated in the study contains more mesoporous, and its specific surface area is smaller than that of the carrier material containing more micropores. At the same time, for the monolithic catalyst carrier, the improvement of the hole capacity of the carrier brings two advantages: Firstly, the larger pore capacity can bear more catalyst slurry and improve the uploading rate of active components; Secondly, large pore volume can increase the accumulation of impurities in the catalytic reaction process, thus prolongs the service life of the monolithic catalyst^[21].

Table 3 Changes of specific surface area and pore properties of cordierite carrier before and after pretreatment

	Surface area(m ² /g)	Pore volume (*10 ⁻³ cm ³ /g)	Pore size(nm)
Without pretreatment	1.0	1.6	28.3
10%HNO ₃ -ordinary	1.7	2.0	17.4
20%HCl-ordinary	1.3	1.9	8.4
20%HCl-heating	10.1	4.4	5.2
10%HCl-heating	10.8	3.9	5.6
10%Citric acid-heating	1.2	1.3	2.3

In order to investigate the removal of acid treatment on the surface impurities of cordierite carrier and the improvement effect of surface morphology, the cordierite carrier before and after treatment was selected for the HCl treatment with good treatment effect, and the microsurface morphology characterization test was carried out. The results were shown in Fig.4.

Without acid treatment(Fig.4a), there were many impurities on the surface of the carrier, the channels were badly blocked and unevenly distributed. At the same time, the specific surface area was small (Table 3) and the surface characteristics of the carrier were not conducive to the uploading of catalyst slurry, and the corresponding uploading rate was also the lowest. As mentioned above (Fig.4), the slurry uploading rate was 12.8%. Through 20% HCl ordinary treatment (Fig.4b), impurities on the surface of the carrier had reduced, but a small amount of impurities remained, which indicated insufficient cleaning. Although most of the channels were exposed, but not clear and uneven. Moreover, due to the presence of a small amount of impurities on the surface, the water absorption rate increased greatly, which affected the experimental results. As could also be seen from Fig.4b, by ordinary treatment, a small part of the carrier surface had been exposed by acid treatment, but the rest was still covered by impurities. After heating with 20% HCl (Fig.4c), the surface impurities of the carrier had been basically cleaned, most of

the carrier had been exposed, and the pores were clear. At this time, the weight loss rate reached 1.1%, and the water absorption rate was 36.8%, which was basically the water absorption effect of the carrier itself. It can be seen from Table 4 that the specific surface area was increased by 10 times, the pore volume was increased by 3 times, and the paste upload rate reached the maximum value, which was 14.5%. In summary, the 20% HCl heating treatment could simultaneously achieve the desired purpose of cleaning the surface impurities of the carrier and improve the specific surface area of the carrier, which was the optimal pretreatment condition for the cordierite carrier.

3.2 Effect of particle size on monolithic catalyst

The particle size of slurry has a certain effect on the upload rate of the catalyst active component. By reducing the particles size of the slurry, the uploading rate and coating uniformity can be improved^[32]. Ball-milling is the most commonly used method to reduce the particle size of slurry^[33]. The effect of ball-milling is mainly affected by the weight ratio of ball-to-powder, rotate speed, time of ball-milling, and so on^[34].

(1). Rotate speed of ball milling

When the rotate speed is very low, the mill can not bring the grinding medium to a certain height, so the grinding medium is almost not taken up, which can only rely on the medium to weak sliding grinding and grinding materials; If the speed of the mill is too high, the inertial centrifugal force of the grinding medium will make the grinding medium stick to the inner wall of the mill and do circular motion together with the mill, also can not reach the purpose of the effective impact of the medium material^[35]. In order to effectively use the grinding and impingement power of the medium in the process of pulverizing, it is necessary to select the speed of the mill according to the actual grinding conditions.

Fig.5(a) showed the size of catalyst slurry (solid content is 10%) prepared by ball grinding (ratio of grinding media to material) for two hours at different rotate speeds. The powder catalyst was screened out through 20 mesh screen. The particle size of catalyst can be greatly reduced by ball milling. When the speed was 300rpm, the particle size of catalyst in the slurry was 3.89 microns. With the increase of rotational speed, the particle size decreases further. With the rotate speed being of 500rpm, the particle size reached the minimum of 1.87 microns. At this stage, the ball grinding broke the larger catalyst particles. The particles were further sheared under the interaction of the zirconia pellets, which led to the particle decline. When the rotating speed was further increased to 600rpm, the particle size did not decrease further, but increased to a greater extent. This is mainly due to the agglomeration of smaller particles. The main reasons for this phenomenon are as follows^{[36][37]} 1. Surface action of particles The decrease of particle size will increase the specific area of the particle and make the particle in a highly activated state. High interface energy can make small particles easily combine with other small particles and become stable, thus forming larger particles. 2. Brownian movement Because of the fast movement of small particles, small particles often collide with each other when doing Brownian motion. Due to the attraction effect, smaller particles attract each other, thus forming secondary particles. The secondary

particles will continue to collide with other particles to form aggregates with larger particle sizes. 3. Van der Waals' force—The van der Waals force is inversely proportional to the particle diameter. The smaller the particle diameter is, the larger the van der Waals force is, so the particles are more likely it is to be agglomerated. Fig.5(b) showed that the size of slurry could be further reduced after adding silica sol, which still reached the minimum size of 1.01 microns at 500 rotating speed.

Meanwhile, Fig.5(b) also showed the relationship between the size of the slurry and the slurry upload rate. The decrease of particle size in slurry had a certain promoting effect on loading. When the particle size was small, the first layer of particles could be piled up at the orifice and pressed closely with the inner wall of the orifice, and the particles with smaller particle size had larger adsorption capacity and could be better adsorbed on the surface of the carrier, so as to improve the adhesion of the coating. Then, a layer of smaller particles was adsorbed on the surface of the carrier, a second layer of particles would continue to form. The surface formed by small particles was more compact than that formed by large particles, and the surface had smaller holes or even no holes (Fig.6(a)). At the same time, the smaller the particle size of the coating is, the better the specific surface area of the whole catalyst will be, thus, it is advantageous to the catalytic reaction. If the particle size was large, the particles could not accumulate in the interior of the pore, but at the top of the pore. At this time, the coating adhesion was low, and the surface of coating was easy to form a large hole. When the particle size of catalyst in the slurry decreases, it could bring the following two advantages: 1. There is strong adhesive force between slurry coating and cordierite carrier; 2. The catalyst particles loaded on the unit area are more, and the specific surface area is larger, which is more conducive to the catalytic reaction.

In order to investigate the effect of particle size on the coating surface clearly, the coating prepared by slurry with different particle size was scanned by electron microscope. Fig.7 showed the surface conditions of coatings prepared with the slurry of different sizes obtained by ball milling. Particle size had great influence on the surface morphology of the monolithic catalyst. When the rotating speed was 300rpm (Fig.7(a)), the particle size obtained was 3.89 microns, the surface of the prepared coating was very rough, uneven, and the large particles with many holes were obvious. With the rotating speed being increased to 400rpm (Fig.7(b)), the particle size decreased to 2.1 microns, the surface of the coating had significantly fewer holes and larger particles compared to Fig.7(a). When the rotating speed was increased to 500rpm (Fig.7(c)), the minimum particle size obtained was 1.47 microns. The surface of the prepared coating was very smooth, no large particles and holes could be seen. It was further shown that the size of the particle size in the slurry had a great influence on the coating effect. As the rotating speed continued to 600rpm (Fig.7(c)), the agglomeration between small particle sizes was strengthened, which led to the formation of large particles, and large particles and pores appear again on the surface of the prepared coating. The pores on the surface of the coating prepared by the large particles also validate the adsorption framework of the particles on the carrier surface.

3.3 Effect of dispersant on monolithic catalyst

The dispersion of catalyst slurry has great influence on the uniformity of coating in the process of preparing the monolithic catalyst by dipping method. During the impregnation process, if the catalyst slurry was easy to settle, the coating on the lower part of the monolithic catalyst would be thicker, or even block the honeycomb channel, while the coating on the upper part would be uneven or even not covered by the coating. At present, the commonly used dispersion methods are stir dispersion, ultrasonic dispersion and ball mill dispersion. The effects of single stir dispersion and stir+ultrasonic dispersion on dispersion properties were studied in our experiment. PVP and PAA were selected as dispersants.

(1). Sedimentation experiment

Settlement experiment can directly reflect the stability of slurry. By observing the settling effect of TiO_2 carrier suspension prepared by adding different dispersants in different dispersants ways, the dispersion property of the suspension was determined. The more difficult the suspension was to settle, the better the dispersion effect was. The experimental results were shown in the Fig.8, the settling time of all suspensions was 6 hours. The dispersion performance of the suspension after stirring and ultrasonic dispersion was obviously better than that of the simple stirring dispersion, the sedimentation interface of the suspension rose obviously. In the stirring process, the addition of ultrasonic factors could improve the dispersion performance of suspension. With the increase of dispersant concentration, the dispersion effect became better, but the dispersion performance of PAA was better than that of PVP. To PAA-stir+ultrasound, the settlement interface could be clearly seen when PAA concentration was 1-2wt%. However, to PVP-stir+ultrasound, sedimentation interfaces could be seen when PVP concentration was 1-4wt%.

(2). Zeta potential

Zeta potential is a measure of the strength of the repulsive or attractive force between particles^[38]. Zeta potential was used to evaluate the stability of slurry dispersion in our experiment. The smaller the molecules or dispersed particles are, the higher the absolute value of Zeta potential (positive or negative) is, and the more stable the system is^[39]. In other words, dissolution or dispersion can resist aggregation. On the contrary, the lower Zeta potential (positive or negative) is, the more likely it is to condense or condense, that is, the attraction force exceeds the repulsive force, and the dispersion is destroyed and condense or condense (it should be noted that the absolute value of Zeta potential represents its stability, and the positive and negative values represent what kind of charge particles have).

Fig. 9 showed the variation of the zeta potential as a function of the type and concentration of dispersant. In terms of different dispersion methods, when the stirring time was the same, the dispersion property of suspension obtained by adding ultrasonic was better than that of single stirring condition. And PAA had better dispersion performance for suspension than PVP. This was consistent with the phenomenon observed in sedimentation experiments. In general, PAA had better dispersion for TiO_2 suspensions^[40]. The stability of the suspension was optimal when the PAA concentration was 4%, and the Zeta potential was -30mV. With the increase of PAA concentration, the adsorption of PAA on the surface

of TiO_2 particles increased, the electrostatic repulsion between particles increased, the settling volume of suspension decreased, and the stability increased. When the concentration of PAA was 4%, the absolute value of Zeta potential reached the maximum value, the suspension stability was the optimal, and the adsorption of PAA on the surface of TiO_2 particles reached saturation. When the concentration of PAA was further increased, the number of free PAA in the solution increased, which tended to produce bridging effect, resulting in a decrease of Zeta potential and a slight deterioration of suspension stability.

The dispersion mechanism of PAA to TiO_2 is shown in the Fig.10^[40]. TiO_2 molecules have a strong polarity, because the length of Ti-O bond is short and not equal, this strong polarity is easy to dissociate the hydrolysis of the adsorbed TiO_2 surface to form hydroxyl groups. Under acidic conditions, the hydroxyl group formed on the surface of titanium dioxide will react with hydrogen ions (Fig.11(step)), making the surface of titanium dioxide particles with a positive charge, forming a positive charge center. PAA is an anionic dispersant. When the PH >3, it can ionize and form a large number of RCOO^- ($\text{RCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{RCOO}^- + \text{H}_3\text{O}^+$). The positive charge center on the surface of titanium dioxide particles can adsorb RCOO^- of PAA, the adsorption RCOO^- on the surface increases, the electrostatic repulsion between particles increases, forming an electrostatic stabilization effect, and the Zeta potential increases, the dispersion property of the corresponding suspension is also optimal^[40].

(3). SEM

The stability of slurry has great influence on the uniformity of coating. In order to observe the effect of slurry stability on coating uniformity more clearly, the slurry with different dispersion properties was impregnated with the pretreated cordierite at a volume height just equal to the height of the cordierite carrier. Fig. 11 showed the scanning electron microscope results. The stability of slurry affected the uniformity of coating mainly from two aspects: 1. When the slurry settled in a short period of time (<15min), the coating could not completely cover the cordierite carrier, resulting in the bare leakage part of the carrier, at the same time, the serious cracking of the coating will reduce the adhesion of the coating and the catalytic performance of the monolithic catalyst; 2. For slurry dispersion performance in medium effect, the main defect of the coating is that when the particles are absorbed to the surface of the carrier, a small range of agglomeration will occur, and the final coating will contain many holes of different sizes, because the particles cannot be completely wrapped by the dispersant. The cracking phenomenon is significantly reduced when compared to coatings made of poorly dispersed pastes.

3.4 Catalytic toluene combustion over the coated Pt/Ce- TiO_2 catalyst in the multi-channel microreactor

(1). Effect of pretreatment on catalytic performance

In order to verify whether the cordierite pretreated with acid would affect the catalytic effect of the integral catalyst prepared, the cordierite before and after the acid treatment was used as the carrier to prepare the integral catalyst and investigate its catalytic degradation performance of toluene. As can be seen from Fig.12(a), when the cordierite was pretreated, monolithic catalytic activity of the catalyst increased, with

pretreatment the specific surface area of cordierite and the upload rate of slurry increased, which indicated that acid pretreatment of cordierite would not affect the basic performance. Cordierite pretreated by 20% HCl under heating condition had better low temperature activity. As can be seen from Fig. 12(b), T_{10} of catalytic toluene was 142°C, 10 °C lower than that of unpretreated, and 3~15°C lower than that of other pretreatment methods. As can be seen from Fig. 12(c), T_{90} of catalytic toluene was 200 °C, slightly lower than that of untreated or other pretreatment methods. The specific surface area of the carrier was increased by 10 times and the loading rate was 14.5%, which was the maximum loading rate among all the methods. Moreover, the expansion of the pore volume was conducive to the improvement of the quality of the impurity heap generated during the catalytic reaction. When 10% HCl heated pansy was used as the carrier, the catalytic efficiency was slightly lower than 20% HCl heating treatment. Although the specific surface area of the pansy was relatively high, its water absorption rate and upload rate were both lower than those of 20% HCl heating treatment, which was one of the important reasons for its low catalytic activity. The catalytic activity of the catalysts prepared with 10% HNO₃ was not significantly different from that of untreated cordierite, and the two groups of cordierites had similar specific surface area and upload rate.

(2). Effect of particle size and dispersant on catalytic performance

The toluene catalytic performance of monolithic catalysts prepared with slurry sizes of different sizes was tested, and the results were shown in Fig.13. The catalytic degradation performance of toluene was improved with the decrease of size of slurry. When the particle size of catalyst slurry was 1.01 micron, T_{10} and T_{90} were about 10°C lower than that of monolithic catalyst prepared from 3.03 micron catalyst slurry. At the same time, it was found that the performance of monolithic catalyst prepared by catalyst slurry with dispersant was better than that without dispersant at high temperature. There was no significant difference in its activity at low temperature.

4. Conclusions

The pretreatment of cordierite with 20% HCl can improve the properties of cordierite. The water absorption rate and specific surface area were significantly increased through heating pretreatment. When the coating upload rate was 14.5%, the low temperature catalytic activity of toluene increased. The upload rate was inversely proportional to the size of slurry. Reducing the particle size of catalyst particles in the slurry could increase the loading rate and specific surface area. When the size of slurry decreased from 3.03 micron to 1.01 micron, the loading rate increases by nearly 3%. At the same time, the T_{10} and T_{90} of catalytic degradation of toluene were reduced by about 10 °C. 4% PAA had the best dispersion performance for the slurry. The uniformity of catalyst coating could be improved and the high temperature activity of catalytic degradation of toluene was also enhanced. The catalytic efficiency of the monolayer catalyst increased through the pretreatment of the carrier, the adjustment of the size of the slurry particle and the improvement of the dispersion property of the slurry.

5. Declarations

Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Wenjun Liang, Qinglei Li and Sida Ren. The first draft of the manuscript was written by Qinglei Li, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Competing interest

The authors declare that they have no competing interest.

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7. Tables

Table 4 is not available with this version.

Figures

Figure 1

Process of preparation of monolithic catalyst

Figure 2

Changes of water absorption of cordierite under pretreatment conditions

Figure 3

Changes of upload rate of cordierite under pretreatment conditions

Figure 4

Surface morphology of cordierite carrier before and after acid treatment (×1000)

Figure 5

The particle size obtained at different rotation speeds and the relationship between particle size and the upload rate (a) no additives (b) 25% silica col

(a) 1.47 μm

(b) 2.10 μm

Figure 6

Adsorption model of different particle sizes on cordierite carrier surface ((a).small size;(b).large size)

Figure 7

SEM of the coating prepared by the slurry obtained by ball grinding at different rotational speeds (a.300rpm-3.89μm b.400rpm-2.10μm c.500rpm-1.47μm d.600rpm-3.02μm)

(1) PVP-stir

(2) PVP-stir+ultrasound

(1) PAA-stir

(2) PAA-stir+ultrasound

Figure 8

Effects of different dispersants and dispersants on settling properties of slurry (from left to right, dispersant concentrations being 1,2,3,4,5,10wt%)

Figure 9

Zeta potential of slurry with different dispersion properties

Figure 10

The dispersion mechanism of PAA to TiO₂

Figure 11

Surface morphology of washing coating($\times 250$)

Figure 12

Catalytic activity of toluene for different pretreatment

Figure 13

Catalytic activity of toluene with different slurry sizes and dispersant