



Studies on Preparation and Catalytic Performances of Monolithic Solid Acid Catalysts

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In order to facilitate separation and recycling, a novel $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2/\text{cordierite}$ monolithic catalysts were prepared by dip-coating method and sol-impregnation method. The adherent stability of the catalyst was measured by ultrasonic wave and thermal oscillation. The surface morphology and crystalline structure were separately characterized by SEM and XRD. The acid treatment results showed that the weight loss rate of cordierite support can reach 4.53 % by 30 % oxalic acid solution impregnated for 6 h, which was the suitable acid treatment condition. The study of monolithic solid acid prepared by different methods demonstrated that the catalyst prepared by sol-impregnation method exhibited better adherent and thermal stability than dip-coating method. The weight loss rate was less than 1 % by ultrasonic wave and thermal oscillation and the *n*-butyl acetate esterification yield was 75 %. The SEM images of monolithic catalyst prepared by sol-impregnation method showed that the particle size on the catalyst surface was more uniform and regular. The catalyst prepared by sol-impregnation method appeared a complete anatase TiO_2 and mainly tetragonal ZrO_2 from the XRD spectra.

Key Words: Monolithic solid acid, Catalytic performances, Sol-impregnation, Adherent stability.

INTRODUCTION

In the recent three decades, sulfated metal oxides have attracted intense interest as a catalyst for acid catalyzed reactions^{1,2}. This is mainly due to the distinct advantage of solid super acid catalysts such as easy preparation, high catalytic activity, strong acid strength, high selectivity, environmentally friendly and easy to recover and reuse³. Besides, it can replace the traditional liquid acid catalyst which is widely applied in organic reactions. However, with the application of the catalyst and found that the total acid amount is less than liquid acid and the deactivation due to coking of the catalyst shortens its service life. In addition, the catalyst is powdery resulting in separation and recovery difficulty after reaction, which causes difficulties for industrial applications.

Monoliths are increasingly under development and evaluation for chemical process, refining industries, catalytic combustion, *etc.*^{4,6}. Cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) has a large number of parallel channels, where catalysts are applied. Monoliths offer the advantages of the absence of a need for filtering, low pressure drop, high geometrical surface area, safer operation and the absence of maldistribution problems. Nowadays, the most successful industrial application of monolithic catalysts is the hydrogen peroxide production using the anthraquinone autooxidation process⁷. Beers *et al.*⁸ have

studied the liquid phase esterification of hexanoic acid and 1-octanol in a structured catalytic reactor using zeolite BEA.

In this paper, the $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2/\text{cordierite}$ monolithic catalysts were prepared by dip-coating method and sol-impregnation method using cordierite as support. The catalytic activity for synthesis of *n*-butyl acetate was tested. The physico-chemical properties were investigated by ultrasonic wave, thermal oscillation, SEM and XRD.

EXPERIMENTAL

Catalyst preparation: The $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ (SZT) pulverous solid super acid catalyst was prepared by impregnation-deposition method⁹. Monolithic catalysts were prepared by different methods using SZT as the precursor of the active component. Commercial cordierite with a cell density of 400 cpsi was cut to supports with diameter of 10 mm and length of 20 mm. The cordierite supports were pretreated by oxalic acid solution, washed with deionized water and calcined at 300 °C for 2 h. Then the supports were coated with pseudo-boehmite and urea until the loading of the washcoat was generally 5 wt %. The coated monolith was calcined at 500 °C for 1 h.

Dip-coating method: The washcoat solution of SZT, pseudo-boehmite and urea was made by ball-milling (DC-2) and not milling (DC-1) method. Monolithic catalysts were

prepared by impregnating the coated monolith in the washcoat solution repeatedly until a certain coating amount. Finally, the catalysts calcined at 500 °C for 3 h.

Sol-impregnation method (SI): A certain amount of tetra butyl titanate ethanol solution was added into $ZrO(NO_3)_2 \cdot 2H_2O$ solution under fast stirring. The mixture solution was aged at 70 °C for 3 h when the light yellow sol was formed. The monolith coated with pseudo-boehmite was put in the sol and took out after 30 s. Then dried at 120 °C for 1 h and calcined at 300 °C for 1 h. Repeat the above process until required coated amount. Finally, the monolith was impregnated in 1M $(NH_4)_2SO_4$ for 12 h and then calcined at 500 °C for 3 h. The formula of coating amount is as follow:

$$\text{Coating amount } \eta (\%) = 100 \times \frac{w_2 - w_1}{w_1}$$

where w_1 is the weight of clean cordierite monolith; w_2 is the total weight of coating and cordierite monolith.

Catalyst characterization

Scanning electron microscopy (SEM): SEM studies were conducted to determine the morphology of the washcoat and the distribution of the active materials on the monolithic catalysts. These measurements were made using a S3400 scanning electron microscope (Hitachi, Japan).

Powder X-ray diffraction (XRD) measurements: Structural characterization of the catalysts were performed by a XD-3A X-ray diffractometer (Shimadzu, Japan), using $Cu K\alpha$ radiation in the range 5-90° (2θ) at a scanning speed of 10 deg/min. The X-ray source was an anode operating at 40 kV and 40 mA, filtered with nickel foil ($\lambda = 1.5418 \text{ \AA}$).

Ability of resistance mechanical shock: The monolithic catalyst in ethanol sealed in the beaker was oscillated from 5 min to 60 min in the ultrasonic cleanser (59 KHz, 50 w). The sample was got out, dried and then determined the weight loss. The ability of resistance thermal shock. The sample was heated to 200 °C for 20 min and immediately quenched in cold water. Then dried the sample and measured the weight loss.

Catalytic activity measurement: The experiments were performed in a three-neck round bottom flask equipped with an efficient mechanical stirrer, a thermometer, a water separator and a tap water-cooled reflux condenser. The monolithic catalyst was fixed on the stirrer blade. The esterification was carried out with an acetic acid/*n*-butanol molar ratio of 1: 3 at 105-110 °C for 4 h. The liquid level of the water separator was controlled as high as the branch pipe. After completion of reaction, the ester layer in the water separator and the reaction solution were mixed in the separatory funnel and successively washed by distilled water, 10 wt % sodium carbonate solution and finally with distilled water. The mixture dried over anhydrous $MgSO_4$ was distilled under 70 mmHg vacuums. Finally, the main product was obtained by collecting the distillate at 52-55 °C.

The extent of conversion for esterification of acetic acid and *n*-butanol was calculated by the following equation:

$$\text{Esterification yield} = (1 - \text{acid value}/\text{initial acid value}) \times 100 \% = [1 - V_{NaOH}(\text{after reaction})/V_{NaOH}(\text{before reaction})] \times 100 \%$$

where " V_{NaOH} " is the volume of the standard NaOH solution (0.1 mol L^{-1}) consumed by titrating the reactant mixture. The acid value is measured by the GB-1668-81 standard method.

RESULTS AND DISCUSSION

Acid treatment of cordierite monolith: The cordierite supports were treated with 30 % of oxalic acid solution at 60 °C for different hours. The weight loss rates of cordierite monoliths were showed in Fig. 1.

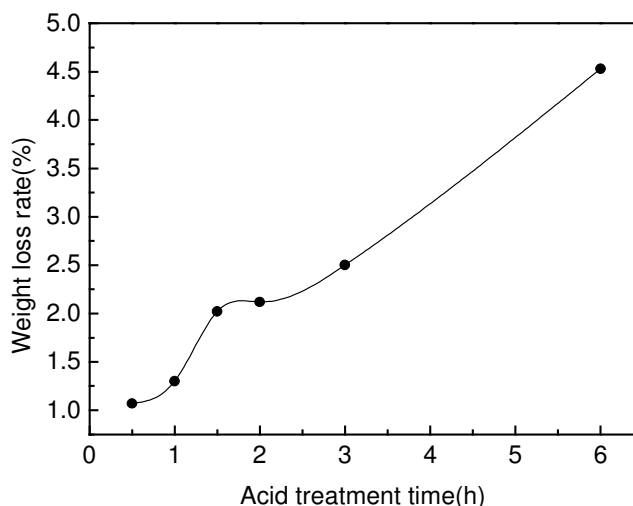


Fig. 1. Weight loss rate of cordierite monolith

As can be seen from Fig. 1, the weight loss rate of cordierite monolith increased gradually with the increase of acid treatment time. After 30 % of oxalic acid treatment for 6 h, the weight loss rate can reach 4.53 %.

Cordierite was a crystalline magnesium aluminosilicate with hexagonal framework and part of the silica was replaced by aluminium in the connected network structure. MgO is alkali, Al_2O_3 exhibits amphoteric and SiO_2 is acid. Thus when cordierite monolith was treated, Mg ions were first removed of corrosion and then were Al ions. This is the reason causing cordierite weightlessness.

Fig. 2 is the SEM image of cordierite monolith treated by 30 % of oxalic acid. Clearly, the surface morphology of cordierite monolith did not change significantly after acid treatment. Shigapov *et al.*¹⁰ used a series of inorganic acids and organic acids to treat cordierite monolith and adopted XRD, XPS, SEM and other characterization tools to study it. The obtained monolith with specific surface area up to $255 \text{ m}^2/\text{g}$ which was due to the acid treatment led to removal of Al and Mg ions from the cordierite structure with formation of pure amorphous silica on the surface of the cordierite.

Adherent stability of monolithic catalysts: The preparation conditions and the coating amounts of monolithic catalysts prepared by different methods were shown in Table-1. Cordierite monolith was firstly coated with about 5 % pseudo boehmite to its surface area which facilitated to coat the active component. Adding a certain amount of urea can prevent the quickly formation of boehmite gel, in order to maintain low viscosity. Besides, it can produce CO_2 and NO gases during calcination, which was beneficial for the formation of porous structure of alumina coating¹¹. As can be seen from Table-1, the required coating times of using ball milling DC-2 method to achieve a certain coating amount was significantly more than DC-1 method. This was because the particle size of

TABLE-1 PREPARATION CONDITIONS OF MONOLITHIC CATALYSTS					
Catalyst	Coating amount of pseudo boehmite (%)	Preparation method	Coating times	Coating amount of active component (%)	
Monolith-1	4.8	DC-1	4	15	
Monolith-2	4.9	DC-1	5	20	
Monolith-3	4.6	DC-2	6	15	
Monolith-4	5.1	DC-2	8	20	
Monolith-5	5.3	SI	5	20	

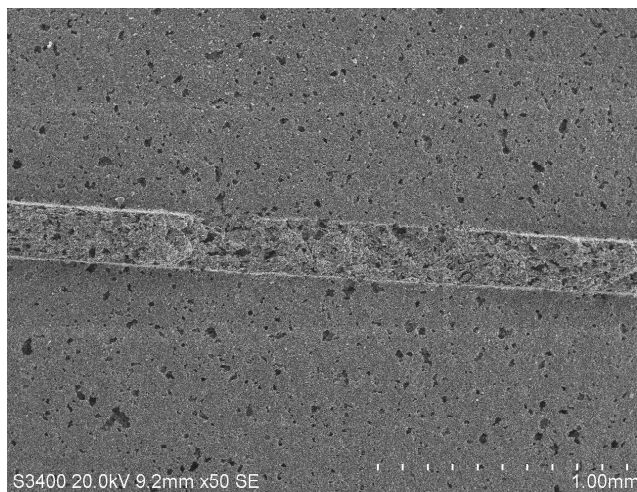


Fig. 2. SEM image of cordierite monolith after oxalic acid treatment

powder catalyst from ball milling was smaller and correspondingly the coating amount was fewer. But this was favour for the adherent stability of the monolithic catalyst. The required coating times to prepare a certain amount of active component catalysts by SI method were as much as DC-1 method.

The weight loss curves with time under ultrasonic vibration were given in Figs. 3 and 4 showed the effect of thermal shock on the weight loss of monolithic catalysts.

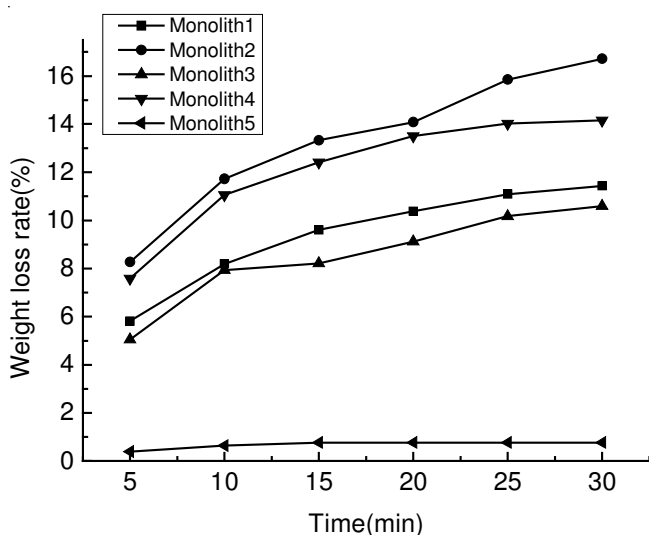


Fig. 3. Weight loss curves with time under ultrasonic vibration

It was observed that all monolithic catalysts showed the same trend in the ultrasound and thermal treatment, namely, the weight loss increased with treatment time and thermal shock times. For both testing methods, the monolithic solid acid catalysts prepared by DC-1 method showed the lowest

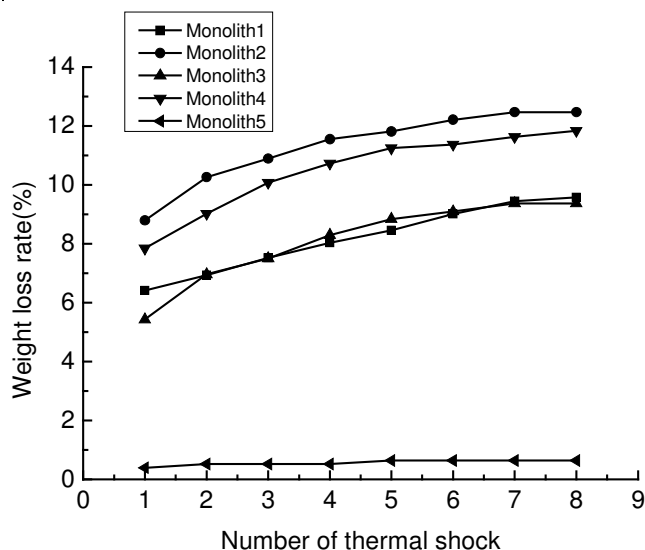
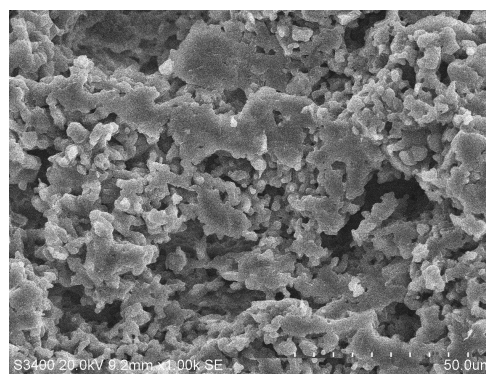


Fig. 4. Effect of thermal shock on the weight loss of monolithic catalysts

adherent stability. The weight loss rates of the catalysts prepared by DC-2 method were slightly lower than DC-1 method. The catalysts prepared by SI method showed the best resistance to mechanical shock and thermal shock with the weight loss less than 1 %. It can also be seen from the figure, the capacity of monolithic catalyst resistance to thermal shock was better than the resistance to mechanical shock. Thus ultrasonic vibration made it easier for the loss of catalytic washcoat.

Observation of surface morphology: The SEM images of cordierite monolith coated with pseudo boehmite in Fig. 5 were, respectively magnified 1000 and 5000 times. It was obvious that many alumina particles formed with particle size from 2-5 μm on the cordierite monolith which was coated with pseudo boehmite. These alumina particles distributed in the pore passages of cordierite, increasing its surface area. And this was helpful for coating active component.



Magnification (× 1000)

Magnification ($\times 5000$)

Fig. 5. SEM images of cordierite coated with pseudo-boehmite

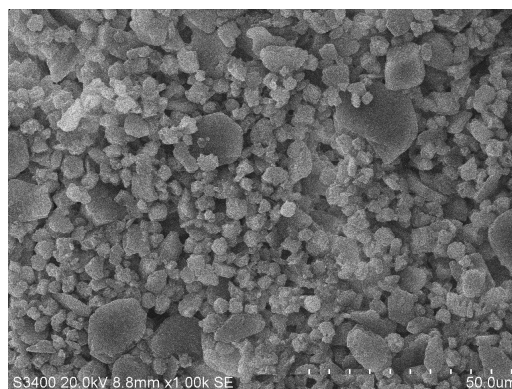
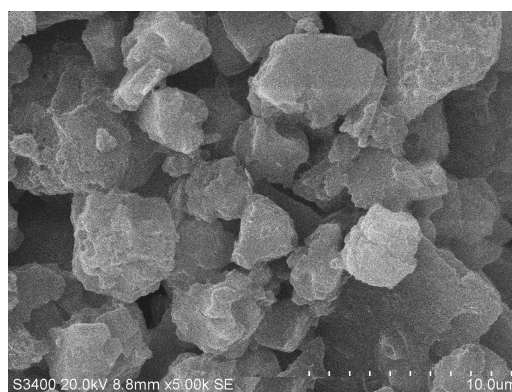
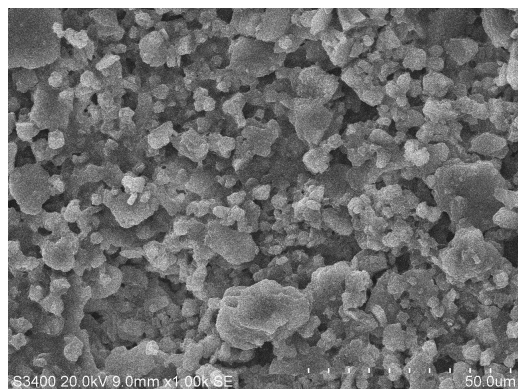
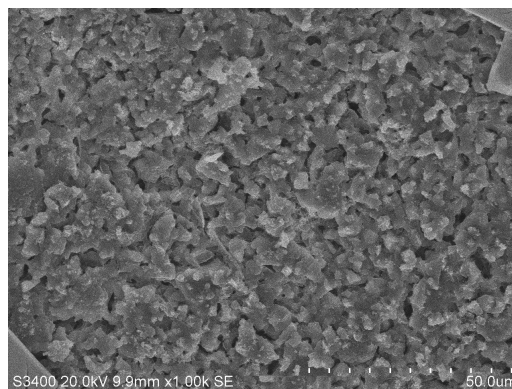
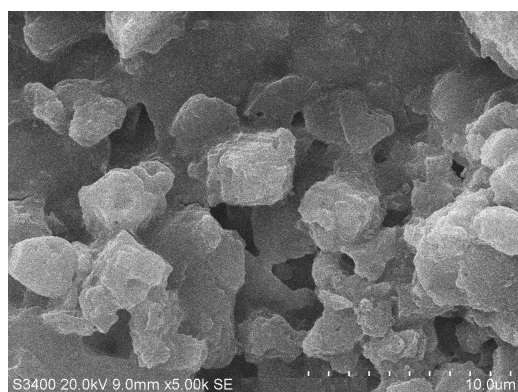
Magnification ($\times 1000$)

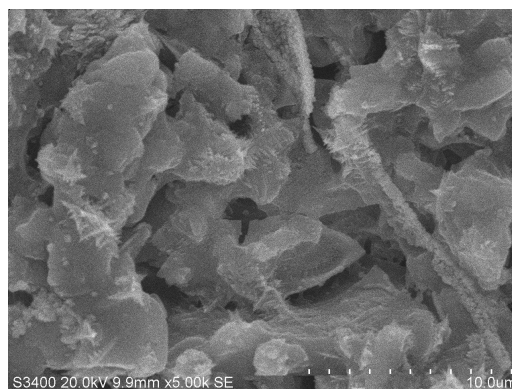
Fig. 6 showed the SEM images of monolithic solid acid prepared by three different methods. It can be seen from the SEM images of monolithic catalysts prepared by the dip-coating method, catalyst particles uniformly distributed in the cordierite support and the surface did not crack. Clearly, the particle size of catalyst by ball milling was smaller and more regular than that without ball milling. And this was the reason for its good adherent stability. Zirconium and titanium oxides layer stagger and density distributed on the surface of monolithic solid acid catalyst which was prepared by sol-impregnation method. From the image magnified by 5000 times can be seen that a large number of whiskers existed on the catalyst surface, which were attributed to zirconium and titanium oxides. The whiskers increased the surface area of the catalyst and were conducive to the improvement of catalytic activity.

Magnification ($\times 5000$)

(b) DC-2

Magnification ($\times 1000$)Magnification ($\times 1000$)Magnification ($\times 5000$)

(a) DC-1

Magnification ($\times 5000$)

(c) SI

Fig. 6. SEM images of monolithic catalysts prepared by different methods

Effect of coating amount on catalytic activity: The monolithic catalysts with coating amount from 10-40 % were prepared by DC-1 method. The coating solution was constituted by 20 mL water, 3 g powder catalyst, 1 g pseudo boehmite and 1 g urea. The results of synthesis of *n*-butyl acetate using the monolithic catalysts were shown in Fig. 7.

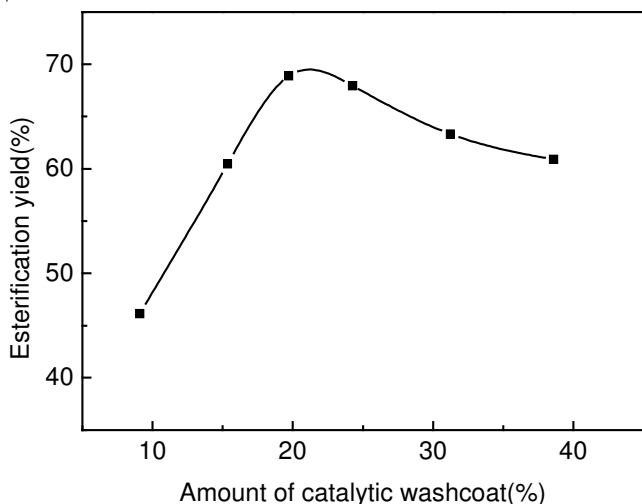


Fig. 7. Effect of washcoat loadings on esterification yield

It can be seen from Fig. 7, the yield of *n*-butyl acetate gradually increased with the increasing of washcoat loadings. When the loadings were 20 %, the esterification yield reached the peak value 68.9 %. But continued to increase the amount of washcoat loadings, the esterification yield declined. This may be because increased the washcoat loadings can increase the active sites of the catalyst surface. But excessive loadings may block the pores, which would reduce the active sites of the catalyst surface. In addition, excessive loadings were unfavourable for the adherent stability of the monolithic catalyst. Therefore, the appropriate amount of washcoat loadings was 20 %.

Comparison of different preparation methods: Monolithic solid acid catalysts with coating amount of 15 and 20 % were, respectively prepared by DC-1, DC-2 and SI method. The results of them used to catalyze the reaction of acetic acid and *n*-butanol were shown in Fig. 8.

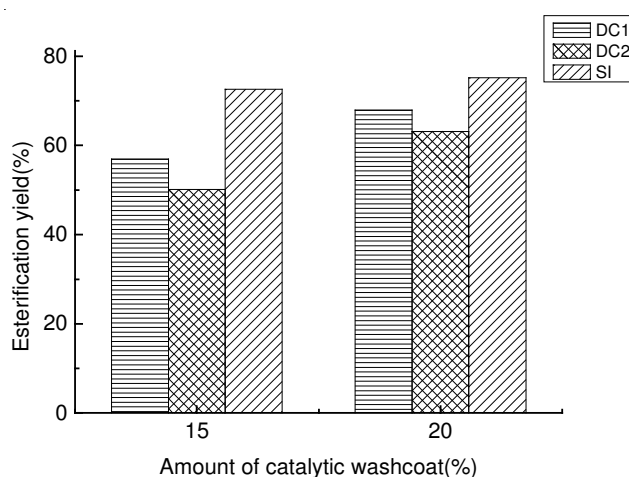


Fig. 8. Catalytic activity of catalysts prepared by different methods

It was obvious that the catalysts prepared by SI method had the highest catalytic activity and the esterification yield was above 70 %. The catalytic activity of monolithic catalyst prepared by DC-1 method was higher than the catalyst prepared by DC-2 method. When the coating amount was 20 %, the esterification yield can reach 68 %.

The catalytic activity of monolithic catalyst prepared by DC-2 method was relatively low, probably because the ball milling process destroyed the pore structure and the surface defects of the catalyst were easy to disappear in the ball milling process, resulting in the decrease of catalytic activity¹². Besides, the ball milling process took a long period, which was negative for industrial production. Thus compared to DC-2 method, the SI and DC-1 methods had advantages in terms of industrial production and catalytic activity. In particular, monolithic catalysts prepared by SI method showed an excellent adherent stability.

Phase structure analysis of monolithic catalyst: Fig. 9 was the XRD patterns of cordierite support and monolithic solid acid catalyst prepared by SI method.

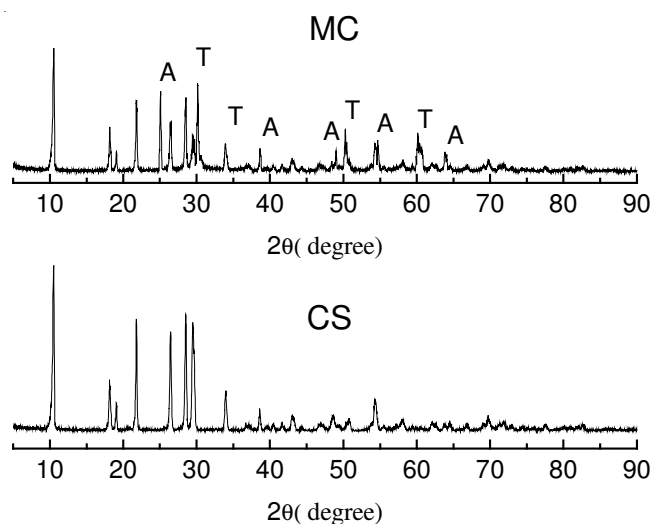


Fig. 9. XRD patterns of the cordierite support (CS) and monolithic catalyst (MC) T-tetragonal phase ZrO_2 ; A-anatase phase TiO_2

The diffraction peaks of cordierite support were consistent with the standard card. But the peak intensity was stronger, indicating a larger particle size of cordierite support. The monolithic solid acid exhibited complete anatase phase (A) peak of TiO_2 , while no rutile phase was observed. So after calcined at 500 °C, the monolithic catalyst formed a perfect anatase phase which was in accordance with the research results of nanometer solid superacid SO_4^{2-}/TiO_2 by Zhan *et al.*¹³.

After impregnated with $(NH_4)_2SO_4$, the intensity of TiO_2 diffraction peak weakened and the peak became to broaden. It showed that the existence of aluminum, zirconium and SO_4^{2-} can prevent the growth of TiO_2 grains and simultaneously increased the specific surface area¹⁴. From Fig. 9 (monolithic-catalyst) can also be seen the metastable tetragonal diffraction peak of ZrO_2 with a weak diffraction peak of monoclinic phase. Metastable tetragonal phase of ZrO_2 had greater activity and can relatively easy to combine more SO_4^{2-} . Obviously, monolithic solid acid catalyst prepared by SI method had stronger

acidity. And this was consistent with the results of catalytic activity for esterification reaction mentioned in the previous section.

Conclusion

Monolithic catalysts were prepared by coating active component on cordierite honeycomb substrate. Thus, the adherent stability and catalytic activity were the main indicators of monolithic catalysts.

(i) The acid treatment results showed that the weight loss rate of cordierite support can reach 4.53 % by 30 % oxalic acid solution impregnated for 6 h, which was the suitable acid treatment condition.

(ii) The SEM images of monolithic catalyst prepared by sol-impregnation method showed that the particle size on the catalyst surface was more uniform and regular. The catalyst prepared by SI method appeared a complete anatase TiO₂ and mainly tetragonal ZrO₂ from the XRD spectra.

(iii) The study of monolithic solid acid prepared by different methods demonstrated that the catalyst prepared by sol-impregnation method exhibited better adherent and thermal stability than dip-coating method. The weight loss rate was less than 1 % by ultrasonic wave and thermal oscillation and the *n*-butyl acetate esterification yield was 75 %.

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