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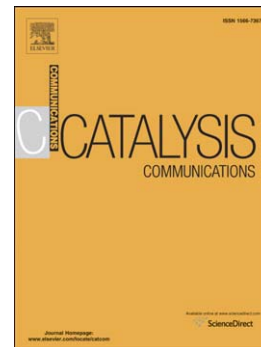
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**Monolithic Cr–V/TiO<sub>2</sub>/cordierite catalysts prepared by  
in-situ precipitation and impregnation for low-temperature  
NH<sub>3</sub>-SCR reactions**

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**Abstract:** Cr–V/TiO<sub>2</sub>/cordierite monolithic catalysts for low-temperature NH<sub>3</sub>-SCR reactions were prepared by in-situ precipitation and impregnation. The adhesion and surface characteristics were examined using ultrasonic oscillation and scanning electron microscopy, respectively. The results showed that the TiO<sub>2</sub> coating adhered well to cordierite by in-situ precipitation. If the loading of the active component, Cr–V, was at least 5.5% by weight, the catalyst achieved excellent SCR activity, with an NO<sub>x</sub> conversion above 90%, in the temperature range 160–300 °C. The Cr–V/TiO<sub>2</sub>/cordierite monolithic catalysts had relatively high stability in the presence of SO<sub>2</sub>.

**Keywords:** Low-temperature NH<sub>3</sub>-SCR, Cr–V/TiO<sub>2</sub>, Monolithic catalysts

## 1. Introduction

Urea-based selective catalytic reduction (SCR) technology is one of the best method for removing  $\text{NO}_x$  in the off-gases of thermal power plants [1,2]. To meet the demands of high throughputs and low-pressure drops in SCR systems available for control of  $\text{NO}_x$  emissions from thermal power plants, monolithic catalysts have become the standard catalyst form [3]. The molding method is the key technology for catalysts used in the SCR process. Extrusion is considered to be one of the most efficient techniques [4,5], and the process involves the following three steps [6]: (a) preparation of powder catalysts, (b) mixing the catalysts with binders, and (c) extrusion. This method is expensive, requires a large amount of powder catalyst, and the preparation process is complicated [7,8]. In addition, the conditions, such as extrusion temperature [9,10], the properties of the raw materials, and the composition of the pastes, strongly affect the properties of the extrudates [11,12], and these conditions must be strictly controlled. Cost-effective catalysts and simplified molding processes are therefore being widely studied to advance SCR technology.

Surface coating methods are one of the latest molding technologies for SCR catalysts [13]. The ceramic cordierite is used as the substrate, and the powder catalyst is loaded evenly on the substrate by surface coating with organic or inorganic binders; this reduces consumption of the powder catalyst. However, the limitations of this method should not be ignored, e.g., the activity of the monolithic catalyst decreases because of the addition of binders [14], there is poor adhesion between the catalyst and the substrate, and adhesion is easily reduced under a high volume of air [15].

In this work, the active component of Cr–V/TiO<sub>2</sub> was adhered on monolithic cordierite by in-situ precipitation and impregnation without any binder. The SCR activities of catalysts with different loadings of the coating and active component were investigated. The adhesion strength and the surface morphologies were examined using ultrasonic oscillation and scanning electron microscopy (SEM), respectively. The results obtained in this study will be useful in the preparation of monolithic SCR catalysts used in the after-treatment of off-gases of thermal power plants.

## 2. Experimental

### 2.1. Catalyst preparation

Commercial honeycomb cordierite monolith of size  $\Phi 15 \times 50$  mm (bore diameter 1 mm) was used as the substrate. First, the cordierite honeycomb (CH) was cleaned for 30 min using ultrasound equipment (China, CKQ5200E). The pretreated cordierite was immersed in a solution of titanium sulfate for 10 min, and then dried at 110 °C for 20 min. The cordierite was then immersed in 25% ammonia solution, and dried at 110 °C for 90 min. This process was repeated several times until the loading was adequate. Finally, the TiO<sub>2</sub>/cordierite was calcined at 550 °C for 5 h.

Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub>, which were used as the sources of Cr and V, respectively, were dissolved in deionized water at a Cr/V molar ratio of 1:4. The TiO<sub>2</sub>/cordierite was impregnated in this solution for 10 min, the residual liquid on the surface was blown away, and then the TiO<sub>2</sub>/cordierite was dried at 110 °C for 2 h and

calcined at 450 °C for 3 h. The catalysts are denoted by  $x$ -Cr-V/TiO<sub>2</sub>/CH- $y$ , where  $x$  and  $y$  are calculated as formulae (1) and (2):  $m_0$  is the quality of bare cordierite;  $m_1$  is the quality of TiO<sub>2</sub>/CH;  $m_2$  is the quality of Cr-V/TiO<sub>2</sub>/CH. A powder Cr-V/TiO<sub>2</sub> catalyst was prepared using a wet-impregnation method for comparison, and the TiO<sub>2</sub> support was synthesized, using a previously reported method [16].

$$x = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

$$y = \frac{m_2 - m_1}{m_0} \times 100\% \quad (2)$$

## 2.2. Characterization

The adhesion strength of the TiO<sub>2</sub> coating on the cordierite was tested using ultrasonic vibration [17]. The TiO<sub>2</sub>/CH monoliths were weighed before and after the ultrasonic treatment to determine the loss of TiO<sub>2</sub> coating.

The morphologies of the samples were examined using SEM (Hitachi S-4700 II), with an accelerating voltage of 15 kV. The samples were covered with a thin gold layer to increase their conductivity.

X-ray diffraction (XRD) patterns were obtained using a SCINTAG XTRA diffractometer equipped with a Ni filter and a Cu K $\alpha$  radiation source, and operated at 40 kV and 50 mA. Intensity data were recorded in a  $2\theta$  range from 10° to 80°, with a size step of 0.04°.

## 2.3. Activity measurements

NH<sub>3</sub>-SCR activity measurements were performed in a fixed-bed quartz reactor from 80 °C to 300 °C, with a total flow rate of 500 mL min<sup>-1</sup>. The typical reactant gas

composition was as follows: 500 ppm NO, 500 ppm NH<sub>3</sub>, 5% O<sub>2</sub>, 0.01% SO<sub>2</sub> (when used) and N<sub>2</sub>. The conversions of NO, NO<sub>2</sub>, O<sub>2</sub>, and SO<sub>2</sub> were monitored continuously using a TESTO350-XL gas analyzer.

### 3. Results and discussions

#### 3.1. Characterization of catalysts

Fig. 1(a) shows that the bare cordierite has a scraggly surface with many irregular pores. This is favorable for adhesion between the coating and the substrate [18]. The SEM image after loading the TiO<sub>2</sub> coating (Fig. 1b) shows a surface with many cracks instead of the original surface, indicating the presence of a TiO<sub>2</sub> layer. The cracks on the TiO<sub>2</sub> layer are favorable for adsorption of Cr and V ions. As shown in Fig. 1(c), a uniform layer of catalyst covering the coating was formed in the final sample, and the irregular cracks on the TiO<sub>2</sub> layer disappeared.

The difference between traditional methods and the in-situ precipitation was the alkaline treatment of the coating. The TiOSO<sub>4</sub> on the surface was alkalized to TiO(OH)<sub>2</sub> by ammonia, and then decomposed to TiO<sub>2</sub> by calcination. The preparation parameters are summarized in Table 1. TiO<sub>2</sub>/CH-A represents the samples with alkaline treatment, and TiO<sub>2</sub>/CH-D represents the samples without alkaline treatment. For the same frequency of coating loading (three times), the mass increase rate of TiO<sub>2</sub>/CH-D was 5.2%, whereas the mass increase rate of TiO<sub>2</sub>/CH-A was 10.1%, twice as much as in the former case. This indicated that the alkaline treatment increased loading of the TiO<sub>2</sub> layer.

From the appearance of the samples after ultrasonic vibration (see table 1), the

TiO<sub>2</sub> layers on the TiO<sub>2</sub>/CH-A samples decreased a little, but were strongly adhered to the cordierite surface, whereas the TiO<sub>2</sub> layers on the TiO<sub>2</sub>/CH-D samples were shed, with a mass loss of more than 10%. This clearly shows that the TiO<sub>2</sub> layer was coated more firmly and uniformly on the cordierite using in-situ precipitation technology. The adhesion in the Cr-V/TiO<sub>2</sub>/CH samples was stronger because loading of the Cr-V active component improves adhesion between the coating and cordierite, and effectively prevents shedding of the TiO<sub>2</sub> coating.

The BET surface areas of the catalytic materials are given in Table 1. Compared with the BET surface area of the bare cordierites (1.70 m<sup>2</sup>/g), rapid increases in BET surface area (8–11 m<sup>2</sup>/g) were found after loading of TiO<sub>2</sub> on the cordierite surfaces, which indicated that the TiO<sub>2</sub> coating has high surface area, and is favorable for Cr-V loading. However, there was little difference in the surface area between the Cr-V/TiO<sub>2</sub>/CH catalysts with different Cr-V loadings.

The XRD patterns of the powder and monolithic catalysts are shown in Fig 4. The XRD results of all Cr-V/TiO<sub>2</sub>/CH monoliths show intense diffraction peaks assignable to cordierite phase. A weak peak of TiO<sub>2</sub> anatase was also detected at  $2\theta = 25.8^\circ$ . However, there were no peaks for the Cr-V oxide active components because of its low loading, and possible coverage by the peaks of the cordierite phase. We could not obtain useful information about the Cr-V phase from the Cr-V/TiO<sub>2</sub>/CH catalysts with different loadings. Therefore, the Cr-V/TiO<sub>2</sub> powder catalysts were employed for XRD characterization. It is seen in Fig. 4(b) that powder catalysts with Cr-V loadings of 5 % and 10 % had no characteristic diffraction peaks from Cr and V



oxide species. This indicated that Cr–V was highly dispersed on the surface. When the Cr–V loading increased to 20 % and 50 %,  $V_2O_5$  and composite oxide ( $Cr_2V_4O_{13}$ ) phases were detected.

### 3.2. $NH_3$ -SCR activities

The effect of the  $TiO_2$  support loading for SCR activity is shown in Fig. 2(a). The activities of samples coated with  $TiO_2$  were much higher than those of samples without the  $TiO_2$  coating. This was assumed to be helpful to achieve high dispersion of the active component on the  $TiO_2$  coating surface [19], thus increasing the SCR activities of the monolithic catalysts. The catalyst with a  $TiO_2$  coating of 10% achieved the best catalytic performance, with an  $NO_x$  conversion above 90% at 160 °C. The SCR activities of samples with  $TiO_2$  loading greater than 10% were almost the same as that of the sample with a 10% loading, which indicated that the internal  $TiO_2$  could not be fully used. Excessive loading of  $TiO_2$  reduces the adhesion strength of the coating; the ideal loading of the  $TiO_2$  coating is about 10%.

With the  $TiO_2$  loading controlled to 10%, the effect of Cr–V loading was also investigated, as shown in Fig. 2(b). The monolithic catalyst with 5.5% loading of Cr–V achieved the highest activity, with an  $NO_x$  conversion above 90% in the temperature range 160–300 °C. This indicated that at a Cr–V loading of 5.5%, the best dispersion was achieved, giving a complete monolayer on the surface of the monolithic catalyst, resulting in the best catalytic activity.

To further investigate the effect of loading of the Cr–V and the feasibility of the in-situ precipitation technology, a powder Cr–V/ $TiO_2$  catalyst was used for

comparison. Cr–V/TiO<sub>2</sub> (1.0 g) was diluted with quartz sand and the results of the activity tests on powder samples are presented in Fig. 3. It can be seen that the sample with a Cr–V active component loading of 10% gave the best SCR performance, the same as the highest activity for the monolithic catalyst. The combination of XRD results and catalytic activity, we consider that both V<sub>2</sub>O<sub>5</sub> and Cr<sub>2</sub>V<sub>4</sub>O<sub>13</sub> are unfavorable for SCR reactions. The optimal loading resulted in a monolayer of Cr–V over the TiO<sub>2</sub> support and was more favorable for SCR activity. Similarly, there is an optimal loading of Cr–V for monolithic catalysts.

### 3.3. Sulfur resistance

The above study shows that a monolithic catalyst with a TiO<sub>2</sub> coating of 10% and a Cr–V active component loading of 5.5% achieved the best SCR activity; the results of sulfur resistance tests on this catalyst at 180 °C and 220 °C, respectively, are shown in Fig. 5. No appreciable decrease was observed in the presence of 0.01% SO<sub>2</sub> at 220 °C in 30 h, although a slight decrease in NO<sub>x</sub> conversion, using the same percentage of SO<sub>2</sub>, was observed at 180 °C. This is because the ammonium sulfates were deposited over the catalyst surface by reaction of SO<sub>3</sub> and ammonia [20].

## Conclusions

It is feasible to prepare Cr–V/TiO<sub>2</sub>/CH monolithic catalysts by in-situ precipitation combined with impregnation, without the addition of any binder. The process is simple and cost-effective. The Cr–V/TiO<sub>2</sub>/CH monolithic catalysts matched the best SCR performances of powder Cr–V/TiO<sub>2</sub> catalysts, and had relatively high sulfur resistance. This in-situ precipitation technology for the preparation of

monolithic SCR catalysts has potential industrial applications.

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### Figure captions

**Fig. 1.** SEM images of different samples: (a) CH (cordierite honeycomb); (b) TiO<sub>2</sub>/CH-10%; and (c) 5.5%-Cr-V/TiO<sub>2</sub>/CH-10%.

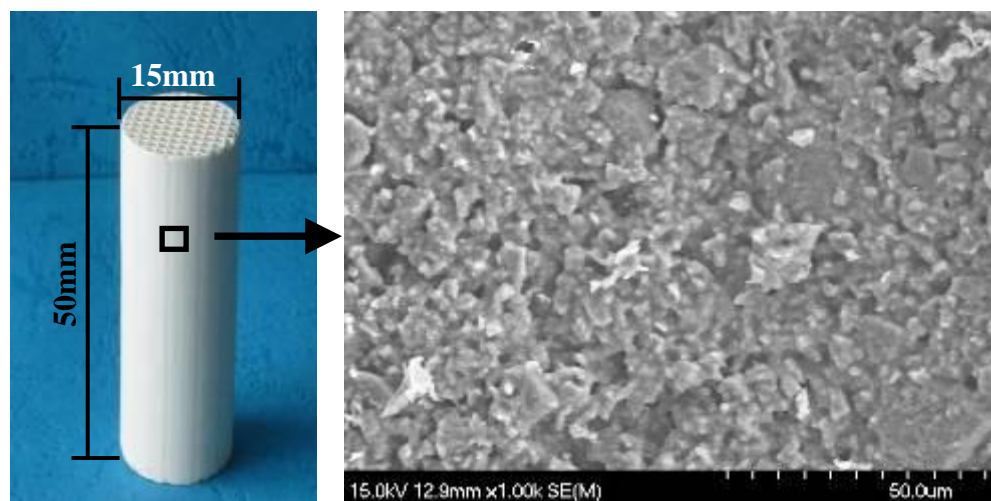
**Fig. 2.** (a) SCR activity of Cr-V/TiO<sub>2</sub>/CH catalysts with different TiO<sub>2</sub> loadings; (b) SCR activities of Cr-V/TiO<sub>2</sub>/CH catalysts with different Cr-V loadings [ $\varphi(\text{NO}) = \varphi(\text{NH}_3) = 0.05\%$ ;  $\varphi(\text{O}_2) = 5\%$ ; gas hourly space velocity = 4000 h<sup>-1</sup>].

**Fig. 3.** NO<sub>x</sub> conversion over powder catalysts with different Cr-V loadings [ $\varphi(\text{NO}) = \varphi(\text{NH}_3) = 0.05\%$ ;  $\varphi(\text{O}_2) = 5\%$ ; N<sub>2</sub> as balance gas; gas hourly space velocity = 60 000 mL h<sup>-1</sup> g<sup>-1</sup>].

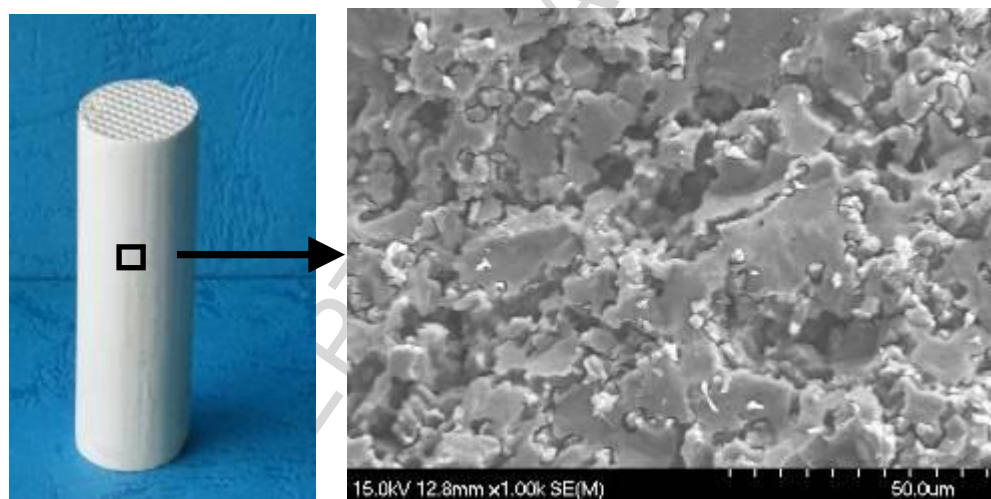
**Fig. 4.** XRD patterns of (a) monolithic Cr-V/TiO<sub>2</sub>/CH catalysts and (b) powder Cr-V/TiO<sub>2</sub> catalysts.

**Fig. 5.** NO<sub>x</sub> conversion of 5.5%-Cr-V/TiO<sub>2</sub>/CH-10% in the presence of SO<sub>2</sub> [ $\varphi(\text{NO}) = \varphi(\text{NH}_3) = 0.05\%$ ;  $\varphi(\text{O}_2) = 5\%$ ;  $\varphi(\text{SO}_2) = 0.01\%$ ; gas hourly space velocity = 4000 h<sup>-1</sup>; reaction temperature: 220 °C and 180 °C].

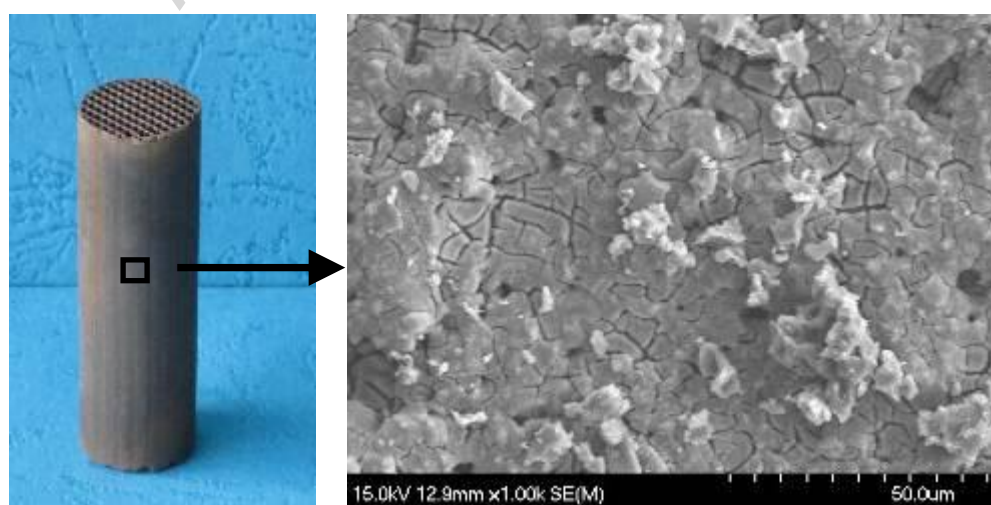
&lt;Figure 1&gt;



(a)

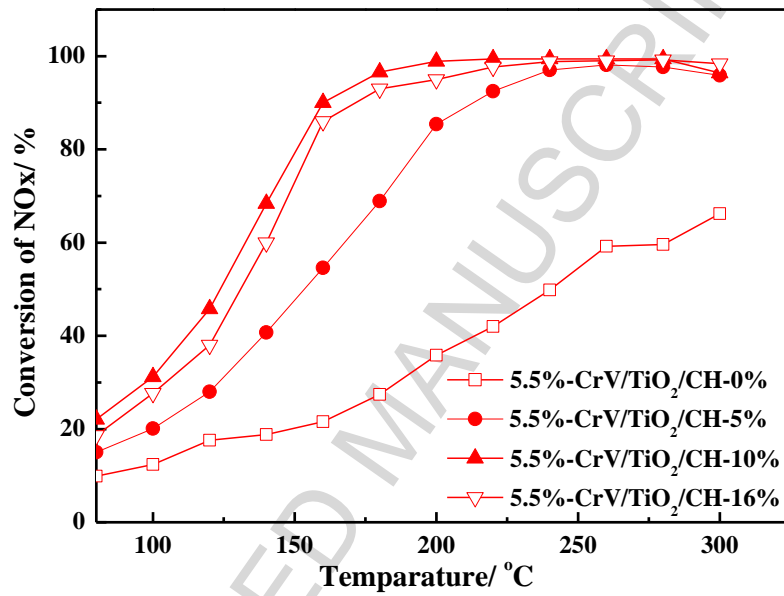


(b)

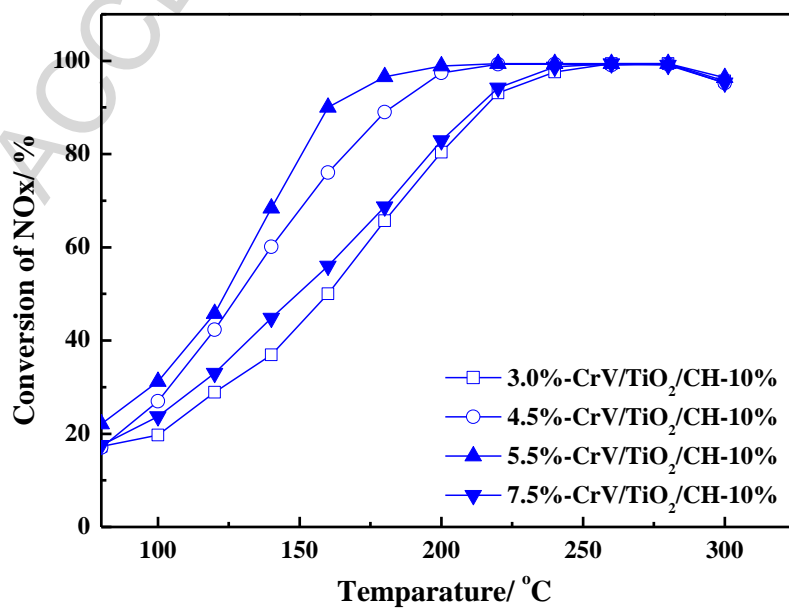


(c)

&lt;Figure 2&gt;

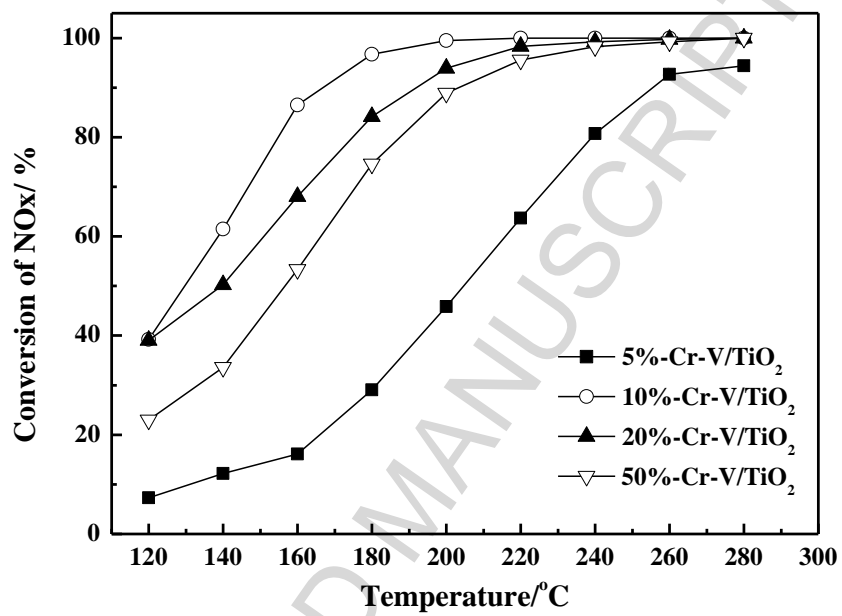


(a)

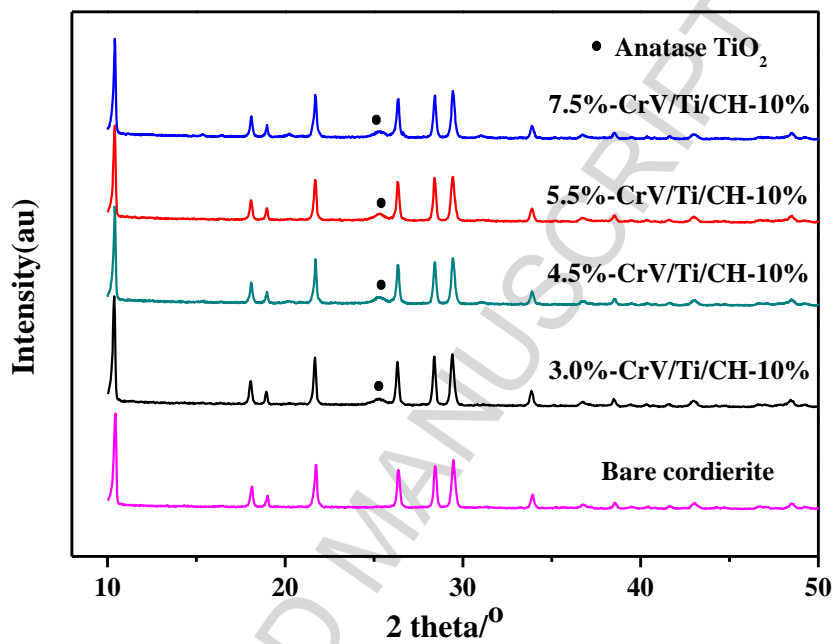


(b)

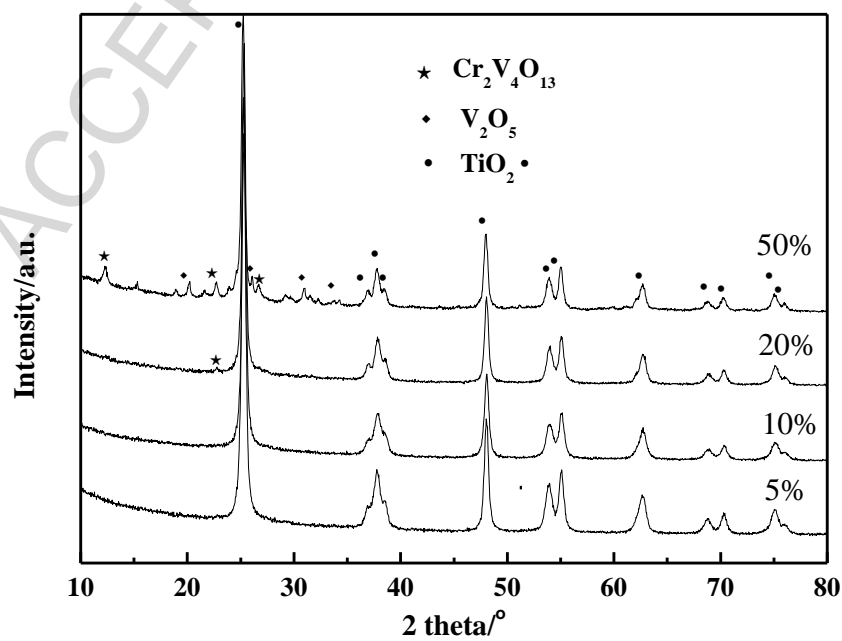
&lt;Figure 3&gt;



&lt;Figure 4&gt;



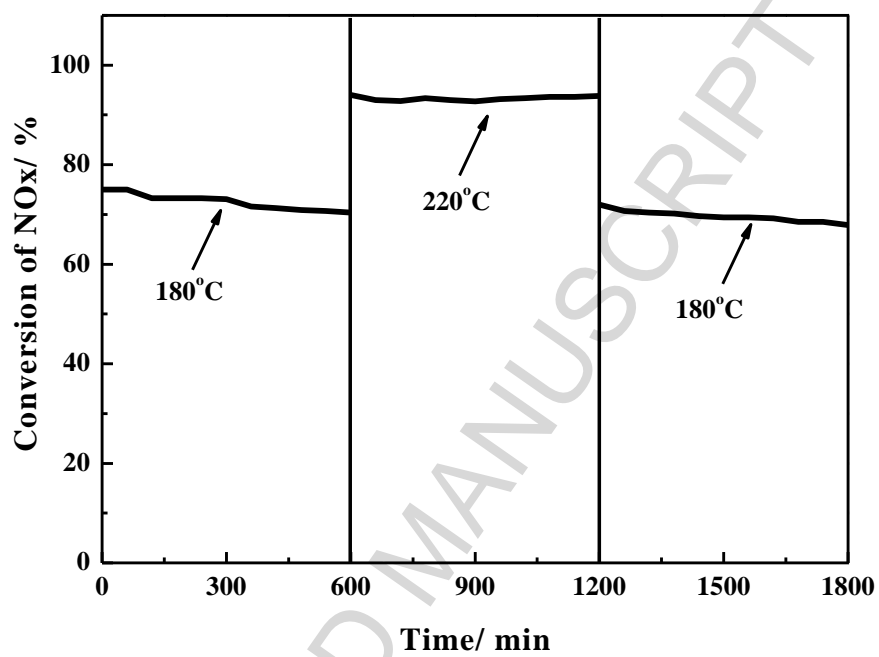
(a)



(b)



&lt;Figure 5&gt;



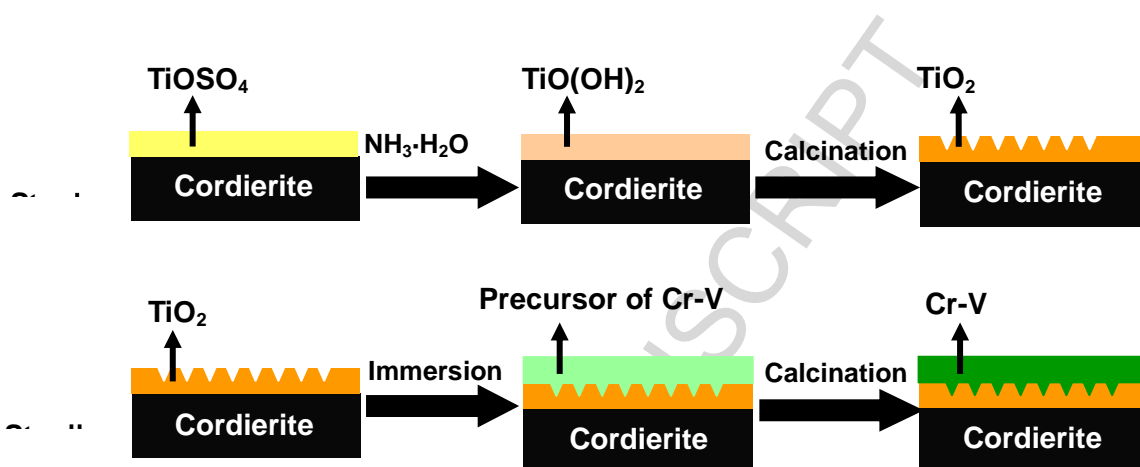
**Table 1**

Preparation parameters and results of mechanical stability tests.

Samples	$m_0(\text{g})^c$	TiO <sub>2</sub> Loading (wt%)(N <sup>d</sup> )	TiO <sub>2</sub> Loss (wt%)	Cr-V loading (wt%)	Mass Loss of monolithic catalyst (wt%)	$S_{BET}$ (m <sup>2</sup> /g)
Bare Cordierite(CH)	7.0	/	/	/	/	1.70
Ti/CH-D <sup>a</sup>	7.0	5.2(3)	10.2	/	/	/
Cr-V/Ti/CH-D <sup>a</sup>	7.1	5.8(3)	/	4.8	3.0	/
	6.9	6.0(3)	/	4.6	3.6	/
Ti/CH-A <sup>b</sup>	7.1	7.4(2)	6.1	/	/	8.76
	7.0	10.1(3)	4.9	/	/	10.70
	7.0	12.5(4)	6.8	/	/	11.68
Cr-V/Ti/CH-A <sup>b</sup>	7.1	10.4(3)	/	5.8	1.6	11.50
	7.0	10.8(3)	/	6.3	1.8	12.00
	7.0	10.6(3)	/	4.9	3.3	11.89
	7.0	10.5(3)	/	3.4	4.2	12.04

<sup>a</sup> samples without alkaline treatment ;<sup>b</sup> samples with alkaline treatment;<sup>c</sup> the mass of raw cordierite;<sup>d</sup> N: the frequency of coating loading;

## Graphical Abstract



**Research Highlights**

1. TiO<sub>2</sub> coating prepared by binder-free in-situ precipitation adhered well to cordierite.
2. Adhesion was enhanced by loading of Cr–V active component.
3. Excellent SCR activity was obtained for a Cr–V loading of 5.5 wt%.
4. NO<sub>x</sub> conversion above 90% in the temperature range 160–300 °C was achieved.
5. Cr–V/TiO<sub>2</sub>/cordierite monolithic catalysts had high stability in the presence of SO<sub>2</sub>.

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