

# PCDD/F removal at low temperatures over Vanadium-based catalyst: insight into the superiority of mechanochemical method

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## Research Article

**Keywords:** PCDD/F removal, PCDD/F catalytic degradation, 1,2-DCBz, VO<sub>x</sub>/TiO<sub>2</sub> catalyst, mechanochemical, ball-milling parameters

**Posted Date:** May 13th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-463575/v1>

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**Version of Record:** A version of this preprint was published at Environmental Science and Pollution Research on August 31st, 2021. See the published version at <https://doi.org/10.1007/s11356-021-15477-y>.

# Abstract

The high toxicity and low volatility of PCDD/Fs prevent detailed study of their catalytic degradation removal characteristics. In this study, firstly, 1,2-dichlorobenzene (1,2-DCBz) was initially used as a model to investigate the catalytic characteristics of various vanadium-based catalysts prepared by different methods. Then, the optimized catalyst was used for catalytic degradation of real PCDD/Fs at low-temperatures based on a self-made stable source. The  $\text{VO}_x/\text{TiO}_2$  catalysts synthesized by the mechanochemical method (VTi-MC2) had a higher 1,2-DCBz removal efficiency (> 85%) and stability (> 420 min) at low temperatures (< 200 °C) compared to VTi-SG (sol-gol method) and VTi-WI (wetness impregnation method). The physico-chemical properties of catalysts were studied using comprehensive characterization. It was found that the VTi-MC2 has better  $\text{VO}_x$  species distribution and possesses the highest  $\text{V}^{5+}$  species and surface adsorbed oxygen content, which are the key factors contributed to the higher removal efficiency. Accordingly, the mechanochemical method can be used to control the physico-chemical properties of catalyst by adjusting the milling parameters. The optimum ball-milling time is 2 h and the suitable precursor is  $\text{NH}_4\text{VO}_3$  for  $\text{VO}_x/\text{TiO}_2$ . Moreover, the removal efficiency of gas phase PCDD/Fs catalyzed by VTi-MC2 is 97% within a temperature range below 200 °C, and the catalytic degradation of PCDD/Fs surges to 50%, which is higher than those reported research. In general, the mechanochemical strategy reported provides a means for seeking more efficient catalysts used for low-temperature degradation of various trace organic pollutants.

## 1. Introduction:

The emission control of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in incineration flue gas has aroused widespread attention in recent years. Although the emissions of PCDD/Fs species are trace, their extreme toxicity and very low volatility tend to cause massive damage to the bio-system. Hence, the PCDD/Fs are listed as Persistent Organic Pollutants (POPs) in the Stockholm Convention on Persistent Organic Pollutants (POPs) (Yang et al. 1999). Particularly, with the implementation of more stringent standards for dioxin emissions from incinerators, it is urgent to develop and improve the control technology. Usually, model compounds, such as chlorobenzenes, chlorophenols, or furans are used in the research of catalytic decomposition of dioxins(Bertinchamps et al. 2005, Chin et al. 2009, Wang et al. 2015). They have a similar structure to dioxins, yet are easier and safer to handle. Further, these compounds also exist in MSWI flue gas (Everaert &Baeyens 2002, Oh et al. 2021) and are possible precursors in the dioxin formation process(Cieplik et al. 2006, McKay 2002).

Compared with the commonly used adsorption technology, catalytic degradation technology can completely decompose dioxins without causing secondary pollution, which is considered as a potential terminal control technology(Yu et al. 2016). Vanadium-based catalysts are especially acknowledged in the study of catalytic degradation of dioxin and dioxin-like compounds due to their potentially high oxidation activities and excellent resistance against chlorine poisoning.(Bertinchamps et al. 2006,

Delaigle et al. 2009a) However, the active temperature of common vanadium-based catalysts for PCDD/Fs degradation (200–350 °C) is higher than the temperature of the flue gas section in the installed catalytic unit (generally < 200 °C)(Chang et al. 2007, Du et al. 2018b). Thus, preparing a more efficient and environmentally friendly catalyst that can be used under low temperature conditions for the removal of PCDD/Fs is urgently needed.

Due to the trace concentrations, low volatility and extreme toxicity of dioxins, it is difficult for general researchers to generate a stable gaseous dioxin and control its concentration under laboratory conditions. This, hinders the study of its catalytic removal mechanism. Some researchers used low-toxicity dioxin model compounds to replace gaseous dioxins for research.

M. Gallastegi-Villa has studied a  $\text{VO}_x/\text{TiO}_2$  catalyst prepared by wet impregnation for the catalytic removal of  $\text{NO}_x$  with 1,2-DCB as the model PCDD/Fs compound (Gallastegi-Villa et al. 2017, Gallastegi-Villa et al. 2020). And the results showed that when the temperature was below 200°C, the removal efficiency of 1,2-DCB was less than 20%. Wang adopted the sol-gel method to prepare  $\text{VO}_x/\text{TiO}_2$ , and the degradation efficiency of PCDD/Fs at 220°C only reached 26.7% (Wang et al. 2016). Debecker has evaluated vanadium-based catalysts prepared by a classical wet impregnation for the removal of PCDD/Fs. Although the  $\text{VO}_x/\text{TiO}_2$  catalysts exhibit rather good removal efficiencies (about 92%) at 200 °C, unfortunately, the degradation efficiency is unclear (Debecker et al. 2011).

Recently, there has been an increasing interest in the mechanochemical synthesis of heterogeneous catalysts. Compared with the traditional catalyst synthesis method, such as the sol-gel method (SG) and wetness impregnation method (WI), the mechanochemical method (MC) has widely gained attention due to its simple operation and low cost (Baláž et al. 2013, Ralphs et al. 2013). In particular, the attention to the environmental problems caused by the use of solvents makes the study of the mechanization method very urgent (James et al. 2012). During the mechanochemical synthesis, the energy generated in the grinding process can have several positive effects on the catalyst, such as generating crystal defects, reducing the particle size, promoting dispersion of active species, forming new interface, and amorphous transformation (Danielis et al. 2019, Kwon et al. 2013, Muñoz-Batista et al. 2018).

To date, several heterogeneous catalysts have been prepared successfully through the mechanochemical method and used for gaseous POPs removal(Yang et al. 2015, Zhang et al. 2015). Whereas, to the best of our knowledge, few studies have reported the application for removal trace organic contaminants in exhaust gas, especially real dioxins or dioxin-like compounds. Furthermore, the variable ball-milling parameters and mechano-chemical effects affect the application for catalytic degradation.

Therefore, in this paper, mechanochemical method was applied to prepare  $\text{VO}_x/\text{TiO}_2$  catalysts, and the catalytic removal performance of dioxin model compounds 1,2-DCBz as well as dioxins under low temperature conditions were evaluated. It is verified that the  $\text{VO}_x/\text{TiO}_2$  catalyst prepared by a novel solvent-free mechanochemical method display excellent catalytic activity in comparison with catalysts prepared by the conventional wetness impregnation (WI) method and sol-gel (SG) method. Furthermore,

comprehensive characterization techniques were performed to study the physico-chemical properties of catalysts to explore the advantage of the mechanochemical method. The effects of precursors and the ball-milling time on catalyst performances were also investigated.

## 2. Experimental Section

### 2.1 Catalyst preparation

Ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ), vanadium oxide ( $\text{V}_2\text{O}_5$ ), tetrabutyl titanate ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ ), oxalic acid, ethanol, 1,2-dichlorobenzene were purchased from Sinopharm Chemical Reagent Co., China. Nano-TiO<sub>2</sub> powder was bought from Xuanchengjingrui New Material Co., Ltd., China.

A series of VO<sub>x</sub>/TiO<sub>2</sub> catalysts were synthesized by a mechanochemical method. The milling process was performed in a Planetary Ball Mill (QXQM-2I, Changsha TENCAN Powder Technology Co., Ltd, China) with four steel jars (250 mL). In a typical synthesis process of VO<sub>x</sub>/TiO<sub>2</sub>, a mixture of NH<sub>4</sub>VO<sub>3</sub> and nano-TiO<sub>2</sub> powders (based on 5 at% vanadium) were physically mixed together thoroughly. Then, the mixture was put into a stainless steel milling pot with several steel balls. The diameters of the steel balls were 10 mm and 5 mm with weight ratios of 1:1. The weight ratio of mixture and steel balls was 20:1. The milling speed of the Planetary Ball Mill was set as 550 rpm. After ball-milling for a certain period of time (0.5 h ~ 4 h), the resultant sample was obtained after the powder was calcined at 450 °C for 3 h in air, which was denoted as VTi-MC<sub>t</sub> (<sub>t</sub>: ball-milling time). In order to explore the influence of a vanadium precursor, the VTi-MC\* was prepared through the same process with V<sub>2</sub>O<sub>5</sub> powder as the precursor.

For comparison, VO<sub>x</sub>/TiO<sub>2</sub> was also prepared through the conventional wetness impregnation method (WI) and sol-gel method (SG) respectively.

Appropriate amounts of NH<sub>4</sub>VO<sub>3</sub> and oxalic acid (molar ratio 2:1) were dispersed in deionized water at 60 °C under vigorous stirring to form a dark-blue solution. The desired amounts of Nano-TiO<sub>2</sub> powder was then added to the solution and stirred for 0.5 h. After standing in air for 24 h, the mixture was dried at 105 °C for 12 h and then crushed to 100 mesh powder. The obtained catalyst was calcined in a muffle furnace for 3 h at 450 °C, which was denoted as VTi-WI.

C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti (0.2 mol) and acetic acid (40 mL) were dissolved in ethanol (150 mL), and stirred for 30 min to form a suspension. NH<sub>4</sub>VO<sub>3</sub> (1.8 g) was dissolved in deionized water (25 mL) with the addition of oxalic acid (5.8 g) to form a settled orange-yellow solution. Then, it was added to the former suspension dropwise under stirring until a homogenous gel was formed. The resulting gel was standing at room temperature for 24 h, dried at 105 °C for 12 h, and then crushed to fine powder. Finally, the resulting catalyst sample was calcined at 450 °C for 3 h, which was denoted as VTi-SG.

### 2.2 Catalyst Characterization

The Scanning electron microscope (SEM) analysis was performed on a Hitachi S-4800 electron microscope. The BET specific surface areas and pore distribution were measured on a surface area and porosity analyzer (TRISTAR 3020, Micromeritics Instrument Corp USA). Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was conducted on a Xianquan TP-5080 (TP 5080, Xianquan Instrument Corp, China) equipped with a thermal conductivity detector (TCD). X-ray power diffraction analysis (XRD) was performed using PANalytical-X'Pert PRO, Holland. The X-ray photoelectron spectra (XPS) were obtained by an ESCALAB MARK II spherical analyzer using an aluminum-magnesium binode (Al 1486.6 eV, Mg 1253.6 eV) X-ray source. All binding energies were corrected with the reference to the C 1s line at 284.8 eV. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) was conducted in Micromeritics Autochem 2920 apparatus equipped with a TCD detector. Before a TPR run, catalysts were pretreated in Ar at 473 K for 2 hours. TPR was performed in a flow of 10% H<sub>2</sub>/Ar mixture gas at a flow rate of 10 sccm with a temperature ramp of 10 °C /min from 50 to 800 °C.

## 2.3 Activity test

To evaluated the catalytic properties of the catalysts for 1,2-DCBz, the experiment was conducted in a fixed-bed flow device with a quartz tube (inner diameter, 33mm) as the reactor (Figure S1). An appropriate amount of catalysts was placed at the middle of the quartz tube, and fixed by quartz wool. The 1,2-DCBz steam was generated by the bubbling method and N<sub>2</sub> was used as the carrier gas. The gas stream replenished into the reactor adopted 11%O<sub>2</sub> and 89% N<sub>2</sub> as a diluting gas, and was controlled by a mass flow controller (designated as 1,2-DCBz<sub>inlet</sub>). Residual 1,2-DCBz in the effluent gas was collected by ethanol (designated as 1,2-DCBz<sub>outlet</sub>), and analyzed using a chromatographer (Agilent 6890N) with a 30 m column (DB-5) and an electron capture detector. The removal efficiency (RE) was calculated as follows:

$$RE (\%) = (1,2\text{-DCBz}_{\text{inlet}} - 1,2\text{-DCBz}_{\text{outlet}}) / 1,2\text{-DCBz}_{\text{inlet}} \times 100\% \quad (1)$$

The catalytic degradation of gaseous PCDD/Fs over VO<sub>x</sub>/TiO<sub>2</sub> catalysts were conducted in a self-made device as shown in Figure S2. A stable dioxin gas generator (Du et al. 2018a) was employed to supply stable gaseous PCDD/Fs and the initial concentration of gaseous PCDD/Fs (PCDD/F<sub>sinlet</sub>) was detected as 3.20 ng I-TEQ/Nm<sup>3</sup> (average value of three runs, with a standard deviation of 6.8%, as is shown in Table S1). An appropriate amount of the catalyst was loaded into the quartz tube, and fixed by quartz wool and a quartz screen. A gas mixture of 11 vol% O<sub>2</sub> and N<sub>2</sub> (balance) was used as the carrier gas. The total gas flow passing through the reactor was set at 500 ml/min by a mass flow controller (GHSV = 14000 h<sup>-1</sup>).

The test system was kept for 60 min in advance to reach a steady state before taking samples. Then, the vapor phase PCDD/Fs in effluent gas were continuously collected by XAD-2 resin and toluene for 60 min (PCDD/F<sub>outlet</sub>). After each experimental run, the glass tube and the used catalyst were rinsed and Soxhlet was extracted with toluene for the determination of residual PCDD/Fs on the catalyst surface and reactor inner walls (PCDD/F<sub>son-catalyst</sub>). The quantitative detection of PCDD/Fs followed the US EPA method 1613 (US EPA, 1994). In our experiments, the recovery rate of each internal standard ranged from 62–107% and fulfilled the recovery standard of 40–130%.

Only the 17 toxic PCDD/Fs congeners were discussed in this work. The Removal Efficiency (RE), Degradation Efficiency (DE) and Adsorption Efficiency (AE) are defined as follows:

$$RE(\%) = \frac{[PCDD/Fs_{inlet} - PCDD/Fs_{outlet}]}{PCDD/Fs_{inlet}} \times 100 \quad (1)$$

$$DE(\%) = \frac{[PCDD/Fs_{inlet} - PCDD/Fs_{outlet} - PCDD/Fs_{on-catalyst}]}{PCDD/Fs_{inlet}} \times 100 \quad (2)$$

$$AE(\%) = \frac{PCDD/Fs_{on-catalyst}}{PCDD/Fs_{inlet}} \times 100 \quad (3)$$

In which,  $PCDD/Fs_{inlet}$  is the initial PCDD/Fs I-TEQ concentration;  $PCDD/Fs_{outlet}$  presents the PCDD/Fs I-TEQ concentration in the off-gas collected by XAD-2 polymeric resin and toluene;  $PCDD/Fs_{on-catalyst}$  signifies the PCDD/Fs I-TEQ concentration adsorbed on the catalyst surface and the reactor inner walls.

## 3. Results And Discussion

### 3.1 Catalyst characterization

The microstructure of various  $VO_x/TiO_2$  catalysts were first identified by SEM (Fig. 1). It revealed that the VTi-MC sample was loosely accumulated with flaky particles, VTi-WI was contained with randomly spherical particles, and VTi-SG was presented by block morphology without apparent stacked particles. It clearly shows that different preparation methods have influence on the microstructure of the catalyst samples.

The porosity of various samples was then characterized by nitrogen adsorption-desorption isothermal analysis. Figure S3(A) illustrates that the  $N_2$  adsorption-desorption isotherms of the catalysts prepared by three different methods are all typical *Type I*/isotherms, which indicates that these catalyst samples have mesoporous structures(K. S. W. SING & R. A. PIEROTTI 1985). Intriguingly, the hysteresis loops of the three catalysts present a wide variety of shapes, indicating that three catalysts have different specific pore structures. The isothermal curve of the VTi-MC catalyst shows *Type H3* hysteresis loop, demonstrating that the pore structure of the catalyst is slit-shaped and formed by loose accumulation of plate-like particles. The isothermal curve of the VTi-WI catalyst displays a *Type H1* hysteresis loop. This implies that the pore structure of the catalyst consists of agglomerates or compacts of approximately uniform spherical particles in fairly regular array. The isothermal curve of the VTi-SG catalyst exhibits a *Type H2* hysteresis loop, which is a representation of narrow necks and wide bodies pores ('ink bottle' pores) or fine particle accumulation pores in the catalyst. Overall, the nitrogen adsorption-desorption isothermal is in accordance with the SEM results.

What's more, according to Figure S3(B), the pore size distribution of VTi-MC and VTi-SG is concentrated in the range of 3-8nm, while that of VTi-WI is concentrated in the range of 10-45nm. Furthermore, the specific surface areas decrease in the order of VTi-SG ( $133\text{ m}^2/\text{g}$ ) > VTi-MC ( $86\text{ m}^2/\text{g}$ ) > VTi-WI ( $44\text{ m}^2/\text{g}$ ). Furthermore, VTi-SG and VTi-MC have equally higher acidity than VTi-WI.

It is worth noting that the mechanochemical parameters have obvious influence on the physicochemical properties of the VTi-MCt catalysts. Initially, with the increase of ball milling time, the specific surface area of catalyst increases at first and then decreases. When the ball milling time is 2 h, the specific surface area reaches a maximum value of  $86 \text{ m}^2/\text{g}$ . This may be ascribed to the energy generated during ball milling process promoting the formation of a new interface in the catalyst (Ralphs et al. 2013). However, further increasing the milling time to 4 h results in a sharp decrease, possibly owing to the structure collapse. This was confirmed by the following XRD characterization. Previous studies demonstrated that pores of 2–5 nm diameter are in favour of the adsorption of 1,2-DCBz and dioxins(Xujian et al. 2014). According to Figure S3(C), the pore volumes of 2–5 nm diameter rise with the increase of milling time, reach a maximum when the milling time is 2 h, and then decrease as a result of a pore structure collapse.

Similar tendency is also observed on the acidity of these catalysts. As reported by Delaigle,  $\text{VO}_x$  presents a lot of Brønsted acid sites while the support  $\text{TiO}_2$  mainly exhibits Lewis acid sites and only has a small number of Brønsted acid sites (Delaigle et al. 2009b). Therefore, better dispersion of  $\text{VO}_x$  as the milling time increases brings more Brønsted acid sites. However, too long milling time ( $\geq 4 \text{ h}$ ) can cause a collapse of  $\text{TiO}_2$  crystal structures, resulting in a sharp decrease of Lewis acid sites of catalysts.

Vanadium precursors also have significant effects on the specific surface area and pore structure of the catalysts. In order to compare the results of the VTI-MC2 which used  $\text{NH}_4\text{VO}_3$  as a precursor,  $\text{V}_2\text{O}_5$  was selected as a precursor and VTI-MC2\* was prepared through the same method. As shown in Table 1, the specific surface area of the VTI-MC2 was more than 3 times higher than that of VTI-MC2\*. The total pore volume of VTI-MC2 was about 2 times higher than that of VTI-MC2\*. Normally, due to the energy produced during grinding process,  $\text{NH}_4\text{VO}_3$  can decomposed to generate gaseous water and ammonia, which are beneficial to the formation of a well-developed pore structure of the catalyst. This promotes the interaction between vanadium oxide products and support  $\text{TiO}_2$ , and thus forming a  $\text{VO}_x$  supported catalyst. Therefore, the VTI-MC2 catalyst has a larger specific surface area and pore volume. Moreover, the pore volume and total acid content of the VTI-MC2 catalyst in the pore size range of 2-5nm is significantly higher than that of VTI-MC2\*, which is more conducive to the adsorption of 1, 2-dichlorobenzene on the surface of the catalyst.

The above results apparently show that the preparation methods and mechanochemical parameters have great influence on specific surface areas, porosity and acidity of catalysts. This observation inspires us to further investigate their effects on the physicochemical properties of catalysts in detail.

Table 1  
Specifications of the various carbon samples

Material	$S_{BET}$	Pore volume	Pore size(nm)	total acid content*
	(m <sup>2</sup> /g)	(cm <sup>3</sup> /g)		
VTi-SG	133	0.19	5.4	0.374
VTi-WI	44	0.26	26.5	0.088
VTi-MC0.5	38	0.09	12.6	0.075
VTi-MC1	40	0.10	11.3	0.077
VTi-MC1.5	50	0.14	11.1	0.084
VTi-MC2	<b>86</b>	0.19	<b>8.0</b>	0.344
VTi-MC3	57	0.15	11.8	0.080
VTi-MC4	31	0.08	12.5	0.046
VTi-MC2*	27	0.10	16.3	0.102

\* Derived from NH<sub>3</sub>-TPD.

XRD was used to study the crystal structure of various catalyst samples. Figure S4 (A) shows the XRD patterns of VTi-WI, VTi-SG and various VTi-MCt catalysts. The diffraction peaks of VTi-WI and VTi-SG could be well indexed to anatase TiO<sub>2</sub> (JCPDS 21-1272) (Zhang et al. 2015), and no characteristic peaks of V<sub>2</sub>O<sub>5</sub> can be fitted. This indicates that the vanadium oxide species are well dispersed on the support amorphously or the microcrystals are less than 4nm cannot be detected through the XRD(Gannoun et al. 2014).

Moreover, in comparison with VTi-WI and VTi-SG, VTi-MCt catalysts have relatively low intensity of TiO<sub>2</sub> peaks, indicating that the ball milling process may lead to the structure defect of nano-TiO<sub>2</sub>. The increased crystal defects can serve as additional binding sites for VO<sub>x</sub>, which is beneficial to improve the dispersibility of the active component VO<sub>x</sub>. Both anatase TiO<sub>2</sub> and rutile TiO<sub>2</sub> are present in all the catalysts synthesized by ball milling methods. Anatase TiO<sub>2</sub> has a metastable phase structure, which is easily transformed into rutile TiO<sub>2</sub> due to the milling effect(Coste et al. 2007). In particular, the diffraction peak intensity of rutile TiO<sub>2</sub> firstly decreases with the increase of milling time (0.5 h ~ 1.5 h), disappears at 2 h, then reappears at 3h, and increases with prolonging the ball milling time. Meanwhile, the diffraction peak intensity of anatase phase TiO<sub>2</sub> gradually decreased, indicating that the anatase TiO<sub>2</sub> converted into rutile phase during ball milling processes.

More importantly, the ball milling time also has an important effect on the dispersion of the active component VO<sub>x</sub>. When the ball-milling time increased from 0.5h to 1.5h, the diffraction peak intensity of

the  $V_2O_5$  crystal decreased, indicating that the  $V_2O_5$  crystal gradually transformed into microcrystalline or amorphous VO<sub>x</sub>. However, when the ball-milling time reached 2h and 3h, the  $V_2O_5$  crystal peak disappeared, indicating that the VO<sub>x</sub> on the catalyst surface is amorphous or the crystal particle sizes are small, which is lower than the detection limitation of XRD. This is consistent with the study of Kwon et al., that the content of highly active monomeric VO<sub>x</sub> species increased with longer ball milling time (Kwon et al. 2013). But surprisingly, when the grinding time continuously increased to 4h, the diffraction peak of the  $V_2O_5$  crystal with low intensity could be observed in the XRD pattern. This phenomenon may be ascribed to the extensively long ball milling time caused collapse of the crystal structure of TiO<sub>2</sub>. The collapse of the crystal structure is not conducive to the dispersion of VO<sub>x</sub> on the surface of TiO<sub>2</sub>, and the result is also in accordance with the  $S_{BET}$  and pore volume.

Therefore, according to the results, it is reasonable to speculate that the formation process of VO<sub>x</sub> on the surface of the catalyst support during the ball milling process, NH<sub>4</sub>VO<sub>3</sub> thermally decomposes to generate  $V_2O_5$  crystals, and then transform into amorphous VO<sub>x</sub>.

Figure S4(B) shows that obvious  $V_2O_5$  crystals can be observed on the surface of the VTi-MC2\* catalyst prepared with  $V_2O_5$  powder as the precursor, indicating that the dispersion of the active component on the surface of TiO<sub>2</sub> support is poor. According to the literature reports(Kwon et al. 2013), the synthesis of  $V_2O_5$  powder and TiO<sub>2</sub> occurred up to a milling time until 3 h. This may be due to the fact that compared to  $V_2O_5$  powder, the interaction between intermediate produced during ball milling of NH<sub>4</sub>VO<sub>3</sub> (such as  $(NH_4)_2O \cdot 3V_2O_5$ ,  $(NH_4)_2O \cdot V_2O_4 \cdot 5V_2O_5$ ) and TiO<sub>2</sub> is stronger, and it is easier to disperse on the surface of TiO<sub>2</sub>.

To get further insight into the chemical state of the catalysts surface element, XPS investigations were then conducted. Figure 2(a) shows the overlapping V 2p3/2 peak of the different samples. The XPS spectra of V 2p3/2 can be deconvoluted into two peaks assigned to the V<sup>5+</sup> and V<sup>4+</sup> species, which were observed at 517.4 eV and 516.3 eV, respectively. The ratio of V<sup>5+</sup>/(V<sup>5+</sup>+V<sup>4+</sup>) was determined through the calculation of the integrated peak areas of V<sup>5+</sup> and V<sup>4+</sup> species. The oxidation process of organic molecules on the catalyst surface is associated with the reduction of V<sup>5+</sup> to V<sup>4+</sup>. Therefore, a higher V<sup>5+</sup> species ratio is considered to be beneficial to the conversion of 1,2-DCBz and dioxins on the catalyst surface. As the Table S2 shows, the V<sup>5+</sup> ratio of VTi-MC2 is 80%, which is higher than that of VTi-WI (77%) and VTi-SG (72%). It is well known that larger specific surface area is benefits in improving the dispersion of the active component VO<sub>x</sub> species, increasing the probability of contact between vanadium and oxygen in the atmosphere, and thus facilitate the oxidation of vanadium to higher valences. Although the specific surface area of VTi-SG (133m<sup>2</sup>/g) is much larger than that of the other two catalysts, the V<sup>5+</sup> ratio (72%) of VTi-SG catalyst is the lowest. This may because the ink-bottle shaped pores are not conducive to the diffusion of oxygen in the pores of the catalyst and hinder the sufficient contact of vanadium species and oxygen on the catalyst surface.

Figure 2 (b) shows that the O 1s peak of various  $\text{VO}_x/\text{TiO}_2$  samples prepared by different methods, which could be divided into two bands. The sub-bands at 531.3–531.9 eV are assigned to the surface adsorbed oxygen (denoted as  $\text{O}_\alpha$ ), and the sub-bands at 529.3–530.0 eV are attributed to the lattice oxygen (denoted as  $\text{O}_\beta$ ) (Chen et al. 2009). It is clearly showed that the binding energy of O1s peak for VTi-MC2 was lower than that of the other two catalysts about 0.2 eV. On the other hand, VTi-MC2 presents a higher  $\text{O}_\alpha$  ratio of 18% than those of VTi-SG (13%) and VTi-WI (9%). As it is well known that the relatively higher concentration of surface adsorbed oxygen is beneficial for the high oxidation activity (Kang et al. 2007, Zhang et al. 2015). It hints that the interaction between oxygen species and metal-dopant on VTi-MC catalyst surface is strengthened through the mechanochemical process. This leads to more surface oxygen vacancy and the increasing amount of chemisorbed oxygen species. In the process of mechanical milling, the energy generated by the friction and collision of steel balls can precipitate the surface lattice oxygen and produce a large number of oxygen vacancies (Ralphs et al. 2013). Then, oxygen is adsorbed on the surface oxygen vacancy and dissociated to form surface chemically adsorbed oxygen, which could effectively improve the catalytic oxidation activity.

Furthermore, it was found that in the case of VTi-MC, more  $\text{V}^{5+}$  species and  $\text{O}_\alpha$  species were present in the crystalline  $\text{V}_2\text{O}_5$  species formed with increasing milling time. The details are shown in Figure S5. This may be due to the prolonged ball milling time, which helps the vanadium oxide contacts with air, therefore, it is easier to be oxidized to high valence vanadium (Zhao et al. 2009).

To gain further insight into the redox ability of various catalysts,  $\text{H}_2$ -TPR experiments were then conducted, and the results are shown in Fig. 3. The significantly large hydrogen consumption peaks centered at around  $450 \sim 470$  °C were assigned to the reduction of  $\text{VO}_x$  from  $\text{V}^{5+}\text{Ox}$  to  $\text{V}^{4+}\text{Ox}$  (Wang et al. 2018). The relatively weak peaks centered at around  $650 \sim 690$  °C were belonged to the reduction of carbon deposited on the catalyst surface, which was from the residue of organic solvent during the catalyst preparation process. Generally, monomeric or highly dispersed  $\text{VO}_x$  display reduction peaks at lower temperatures than polymeric or bulk-like  $\text{VO}_x$  (Kwon et al. 2013). It is remarkable that, the hydrogen consumption peak of VTi-MC2 was about 20 °C lower than that of VTi-WI, thus demonstrating that the redox ability of VTi-MC2 was stronger than that of VTi-WI. Furthermore, the  $\text{VO}_x$  species of VTi-MC2 are expected to distribute more uniformly on the catalyst surface according to its notably narrower reduction peak.

Figure 3(B) shows the  $\text{H}_2$ -TPR relusts of VTi-MC catalysts with different ball-milling times. The position of the maximum reducing temperature decreased to lower temperature as the ball-milling time increased. This may be due to the crystallite  $\text{V}_2\text{O}_5$  species transformed into monomeric species during ball milling process according to the interaction between  $\text{V}_2\text{O}_5$  and  $\text{TiO}_2$ . According to the previous XRD results, excessively long ball-milling time caused the collapse the  $\text{TiO}_2$  crystal structure. Therefore, this reduced the dispersibility of  $\text{VO}_x$  species, which significantly reduces the total acid content of the catalyst (Table 1).

On the basis of the above comprehensive analysis, compared with the  $\text{VO}_x/\text{TiO}_2$  catalysts prepared by the traditional method, the VTi-MC catalyst prepared by the ball-milling method presents stronger redox ability, more  $\text{V}^{5+}$  species and surface adsorbed oxygen species. This, plays an important role on the degradation of dichlorobenzene at low temperatures. Thus, it is expected that VTi-MC can serve as a promising catalyst.

## 3.2 Catalyst activity

The high toxicity and very low volatility of PCDD/PCDFs prevent a extensive study of their catalytic degradation removal characteristics. Therefore, 1, 2-dichlorobenzene (1,2-DCBz) was used as a model to investigate the catalytic activities of various  $\text{VO}_x/\text{TiO}_2$  catalysts in this study firstly.

Figure 4(A) presented the 1,2-DCBz removal efficiency of various catalysts as a function of temperature. In general, the removal efficiency increased with increasing temperature at the range of 150–300 °C for all the catalysts. Especially, the VTi-MC presents the highest removal efficiency at temperatures lower than 200 °C, which suggests the catalyst prepared by ball-milling method has better low-temperature activity. However, in the range of 200–300°C, the activity of VTi-MC and VTi-WI catalysts was similar, and the activity of VTi-SG catalyst was the lowest.

As is well known, the higher  $\text{V}^{5+}$  species and surface adsorbed oxygen content are the key factor for the high activity. Thus, combined with the XPS characterization results, the highest activity of VTi-MC is ascribed to the highest  $\text{V}^{5+}$  and  $\text{O}_{\alpha}$  content. This is owing to the energy generated during the ball milling process will cause some damage to the  $\text{TiO}_2$  crystal and promote the formation of crystal defects. These crystal defects can provide binding sites for  $\text{VO}_x$  species and promote the dispersion of  $\text{VO}_x$ . Moreover, in the process of ball milling, the energy generated by friction and collision of steel balls can precipitate surface lattice oxygen and produce a large number of oxygen vacancies. And thus, the oxygen in the air can dissociate and adsorb on the surface oxygen vacancy to form surface chemically adsorbed oxygen.

In order to research the influence of ball milling parameters on the catalytic activity, we compared a series of VTi-MC catalysts prepared with different ball-milling time. In Fig. 4 (B), the removal efficiency of 1,2-DCBz increased with the increase of temperature. Firstly, with the increase of ball milling time from 0.5h to 2h, the removal efficiency gradually increased, and that of 1,2-DCBz of VTi-MC2 can reached 85% at 150°C. However, as the milling time continued to increase, the removal efficiency of 1,2-dichlorobenzene showed a downward trend (Figure S6). According to the characterization results, even though the heat generated during the ball milling process causes the formation of  $\text{TiO}_2$  crystal defects, which can be used as additional binding sites for  $\text{VO}_x$ , while extensive long ball milling time will lead to the collapse of  $\text{TiO}_2$  crystal structure and seriously damage the pore structure of the catalyst. Meanwhile, the specific surface area and the amount of acid on the surface of the catalyst increased at first and then decreased with the increase of ball milling time. Accordingly, the ball milling method can be used to control the physicochemical properties of  $\text{VO}_x/\text{TiO}_2$  through adjusting the milling parameters, which can in turn improve the catalytic degradation performance.

The long-term reaction was conducted at 150 °C to test the catalysts stability of VTi-MC2. As shown in Figure S7, the catalytic activity of VTi-MC2 maintained its high 1,2-DCBz removal efficiency during the entire stability test within 420 min. As shown in Figure S8, according to the characterization results (including N<sub>2</sub> adsorption and desorption, XRD, XPS and H<sub>2</sub>-TPR), the physical and chemical properties of the catalyst have no obvious changes before and after application. This implies that the physical and chemical properties of the catalyst are relatively stable. The results indicate that VTi-MC2 is a promising catalyst for practical application.

**Reaction condition:** SV = 20,000 h<sup>-1</sup>, inlet PCDD/Fs = 3.20 ng TEQ/Nm<sup>3</sup>, 1h.

Based on the above results, we adopted the best VTi-MC2 catalyst for the catalytic degradation of gaseous PCDD/Fs. The distributions of the catalytic removal efficiency, degradation efficiency and adsorption efficiency of dioxins at different temperatures were investigated.

As shown in Fig. 5 (A), the removal efficiency of gaseous PCDD/Fs on VTi-MC2 catalyst can reach more than 97% in the temperature range of 160–300 °C. This is mainly due to the well-developed pore structure and strong surface acidity of the VTi-MC2 catalyst. This catalyst can successfully adsorb almost all the toxic dioxins in flue gas to the surface of the catalyst after passing through the catalyst powder fixed bed. The pore size distribution of the VO<sub>x</sub>/TiO<sub>2</sub> catalyst prepared by ball milling is concentrated, and the pore volume in the range of 2-5nm is very large. This pore size is close to the size of dioxins (1-2nm), which is beneficial to the adsorption of dioxins. Moreover, the catalyst also has strong acidity, indicating that the adsorption capacity of the catalyst is strong.

At a low temperature of 160 °C, the adsorption efficiency of the PCDD/Fs total toxic equivalent is 84%, which is much greater than the degradation efficiency (14%). With elevating the temperatures, the residual PCDD/Fs on the surface of the catalyst decreased, while the degradation efficiency of PCDD/Fs increased. On the one hand, when the temperature is low, the proportion of activated PCDD/Fs molecules is small. On the other hand, the redox ability of the catalyst is weak at low temperature. Therefore, when the reaction temperature is low (160 °C), the removal of PCDD/Fs in flue gas mainly depends on the adsorption of catalyst. With the increase of temperature, the proportion of dioxin activated molecules increases as well as the molecular mass transfer, pore diffusion rate and redox ability of the catalyst. The PCDD/Fs molecules that collide with the catalyst surface are more easily oxidized and decomposed. Therefore, the degradation efficiency of PCDD/Fs is improved. It is noteworthy that the catalytic degradation of PCDD/Fs is about 51% at 180 °C, which is higher than those reported research(Gallastegi-Villa et al. 2020, Wang et al. 2016). This confirms that VTi-MC is a potential catalyst for PCDD/Fs degradation at low temperatures.

As shown in Fig. 5 (B), the degradation efficiency of PCDDs is higher than that of PCDFs. This signifies that PCDDs are more easily to be degraded on the surface of VO<sub>x</sub>/TiO<sub>2</sub> catalyst than PCDFs. This may be due to that the PCDFs in the source have more highly chlorinated dioxin congeners. This can produce more lowly chlorinated congeners with higher toxicity through dechlorination processes, resulting in a

higher concentration of PCDFs I-TEQ. In addition, the catalytic removal and degradation efficiency of semi-volatile organic compounds are related to the volatility and redox ability of the compound.(Chang et al. 2008) The increase of the chlorination value will not only increase the molecular redox potential of organic compounds, but also increase the molecular weight and reduce the volatility. Compared with the low chlorinated dioxins, the higher chlorinated dioxins have higher redox potential, so they are more stable and not easily oxidized and decomposed.

It can be seen from Fig. 6 that the relationship between the degradation efficiency of 17 PCDD/Fs congeners and the number of chlorine substitutions is similar under different temperatures. There was not a linear correlation between the degradation efficiency of PCDD congeners and the number of chlorination. When the chlorination value increased from tetrachlorination to hexachlorination, the degradation efficiency of PCDD congeners increased. Meanwhile, when the chlorination numbers continued to increase to octachlorination, the degradation efficiency of PCDDs congeners decreased. The change of the catalytic degradation efficiency of PCDFs congeners with the number of chlorination is similar to that of PCDDs congeners. Firstly, it increases with the increase of the chlorination value, but when the chlorination value increases to octachloride, the removal efficiency decreases. The volatility and redox potential of PCDD/Fs congeners have certain effects on its degradation efficiency. When the number of chlorination is lower than that of hexachloro, the volatility is the dominant factor. With the increase of the number of chlorination, the molecular weight of PCDD/Fs congeners increases and the volatility decreases. It is easier to adsorb to the surface of the catalyst to participate in the reaction, and also increases the degradation efficiency. When the chlorination number is higher than hexachlorination, the redox potential is dominant, with the increase of the chlorination number, the redox potential of PCDD/Fs congeners increases, and the difficulty of oxidation decomposition increases. Therefore, the degradation efficiency decreases with the increase of the chlorination value. In addition, the dechlorination of high chlorinated PCDD/Fs congeners to produce low chlorinated PCDD/Fs congeners is also one of the reasons for the low degradation efficiency of low chlorinated PCDD/Fs congeners.

## 4. Conclusion

In this study, various  $\text{VO}_x/\text{TiO}_2$  catalysts were prepared by the sol-gel method, wet impregnation method and ball-milling method. It is found that the VTi-MC2 synthesized by the ball-milling method exhibits a higher activity for 1,2-DCBz removal at low temperatures than that of VTi-SG and VTi-WI. Furthermore, the VTi-MC2 displays a high 1,2-DCBz removal efficiency (> 80%) during the stability test within 420 min at relatively low temperatures (150 °C). Compared with the other two  $\text{VO}_x/\text{TiO}_2$  catalysts prepared by sol-gel method, wet impregnation method, comprehensive characterizations showed that, VTi-MC2 prepared by ball-milling method had better VO<sub>x</sub> species dispersion. It also possesses the highest V<sup>5+</sup> species and surface adsorbed oxygen content, which are the key contributing factor to the higher 1,2-DCBz removal efficiency. During the process of ball milling, the energy produced by friction and collision of steel balls can increase the probability of contact between vanadium and oxygen in the atmosphere. This facilitates the oxidation of vanadium, and can also precipitate lattice oxygen on the surface and generate a large

number of oxygen vacancies, resulting in high chemisorbed oxygen content on the surface of VTi-MC catalyst. Accordingly, the ball milling method can be used to control the physicochemical properties of  $\text{VO}_x/\text{TiO}_2$  by adjusting the milling parameters, and the optimum ball-milling time is 2 h.

In addition, in the temperature range of 160 ~ 300 °C, the removal efficiency of gas phase PCDD/Fs catalyzed by VTi-MC2 can reach more than 97%. This is mainly due to the well-developed pore structure and strong surface acidity of VTi-MC2 catalyst prepared by ball milling. This catalyst can successfully adsorb almost all toxic dioxins in the flue gas to the catalyst surface. Although, at relatively low temperature (< 200 °C), the adsorption efficiency of the dioxins is much greater than the degradation efficiency. It is remarkable that with the increase of temperature, the degradation efficiency of dioxins is improved.

Therefore, we will continue to develop high-efficiency catalysts for low-temperature degradation of dioxin in the following work. In general, the ball-milling strategy reported here provides a means for seeking more efficiency catalysts used for low-temperature degradation of various trace organic pollutants.

## Declarations

### Authors' contributions

Minghui Tang: conceptualization, investigation, and writing the original draft preparation. Qinlin Ye, Cuicui Du: investigation, methodology, data curation. Chengetai Portia Makwarimba, Yao He: reviewing, editing. Shengyong Lu, Yaqi Peng: investigation, conceptualization.

### Availability of data and materials

All data and materials generated or analyzed during this study were included in this published article and its supplementary information files.

### Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 52006191), the Natural Science Foundation of Zhejiang Province (No. LY21E060007), the National Natural Science Foundation of China (No. 51976192) and the Fundamental Research Funds for the Central Universities.

### Compliance with ethical standards

**Competing interests** The authors declare that they have no competing interests.

**Ethical approval** The paper is a conceptualization and analysis of the published literature on the topic. No human subjects or animals were used in this paper.

**Consent to participate** Not applicable.

**Consent to publish** Not applicable.

## References

- Baláž P, Achimovičová M, Baláž M, Billik P, Cherkezova-Zheleva Z, Criado JM, Delogu F, Dutková E, Gaffet E, Gotor FJ, Kumar R, Mitov I, Rojac T, Senna M, Streletsckii A, Wieczorek-Ciurowa K (2013): Hallmarks of mechanochemistry: from nanoparticles to technology. *Chemical Society Reviews* 42, 7571-7637
- Bertinchamps F, Treinen M, Blangenois N, Mariage E, Gaigneaux EM (2005): Positive effect of NO<sub>x</sub> on the performances of VO<sub>x</sub>/TiO<sub>2</sub>-based catalysts in the total oxidation abatement of chlorobenzene. *Journal of Catalysis* 230, 493-498
- Bertinchamps F, Grégoire C, Gaigneaux EM (2006): Systematic investigation of supported transition metal oxide based formulations for the catalytic oxidative elimination of (chloro)-aromatics: Part I: Identification of the optimal main active phases and supports. *Applied Catalysis B: Environmental* 66, 1-9
- Chang MB, Chi KH, Chang SH, Yeh JW (2007): Destruction of PCDD/Fs by SCR from flue gases of municipal waste incinerator and metal smelting plant. *Chemosphere* 66, 1114-1122
- Chang SH, Yeh JW, Chein HM, Hsu LY, Chi KH, Chang MB (2008): PCDD/F Adsorption and Destruction in the Flue Gas Streams of MWI and MSP via Cu and Fe Catalysts Supported on Carbon. *Environmental Science & Technology* 42, 5727-5733
- Chen L, Li J, Ge M (2009): Promotional Effect of Ce-doped V<sub>2</sub>O<sub>5</sub>-W<sub>0</sub><sub>3</sub>/TiO<sub>2</sub> with Low Vanadium Loadings for Selective Catalytic Reduction of NO<sub>x</sub> by NH<sub>3</sub>. *The Journal of Physical Chemistry C* 113, 21177-21184
- Chin S, Jurng J, Lee J-H, Moon S-J (2009): Catalytic conversion of 1,2-dichlorobenzene using V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts by a thermal decomposition process. *Chemosphere* 75, 1206-1209
- Cieplik MK, De Jong V, Bozovič J, Liljelind P, Marklund S, Louw R (2006): Formation of Dioxins from Combustion Micropollutants over MSWI Fly Ash. *Environmental Science & Technology* 40, 1263-1269
- Coste S, Bertrand G, Coddet C, Gaffet E, Hahn H, Sieger H (2007): High-energy ball milling of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> powders. *Journal of Alloys and Compounds* 434-435, 489-492
- Danielis M, Colussi S, de Leitenburg C, Soler L, Llorca J, Trovarelli A (2019): The effect of milling parameters on the mechanochemical synthesis of Pd–CeO<sub>2</sub> methane oxidation catalysts. *Catalysis Science & Technology* 9, 4232-4238
- Debecker DP, Delaigle R, Hung PC, Buekens A, Gaigneaux EM, Chang MB (2011): Evaluation of PCDD/F oxidation catalysts: Confronting studies on model molecules with tests on PCDD/F-containing gas stream. *Chemosphere* 82, 1337-1342
- Delaigle R, Debecker DP, Bertinchamps F, Gaigneaux EM (2009a): Revisiting the Behaviour of Vanadia-Based Catalysts in the Abatement of (Chloro)-Aromatic Pollutants: Towards an Integrated Understanding.

Topics in Catalysis 52, 501

Delaigle R, Debecker DP, Bertinchamps F, Gaigneaux EM (2009b): Revisiting the Behaviour of Vanadia-Based Catalysts in the Abatement of (Chloro)-Aromatic Pollutants: Towards an Integrated Understanding. Topics in Catalysis 52, 501-516

Du C, Ji L, Peng Y, Tang M, Cao X, Lu S (2018a): Catalytic decomposition of PCDD/Fs on a V2O5-WO3/nano-TiO<sub>2</sub> catalyst: effect of NaCl. Environmental Science and Pollution Research 25, 15474-15483

Du C, Lu S, Wang Q, Buekens AG, Ni M, Debecker DP (2018b): A review on catalytic oxidation of chloroaromatics from flue gas. Chemical Engineering Journal 334, 519-544

Everaert K, Baeyens J (2002): The formation and emission of dioxins in large scale thermal processes. Chemosphere 46, 439-448

Gallastegi-Villa M, Aranzabal A, González-Marcos JA, González-Velasco JR (2017): Tailoring dual redox-acid functionalities in VO<sub>x</sub>/TiO<sub>2</sub>/ZSM5 catalyst for simultaneous abatement of PCDD/Fs and NO<sub>x</sub> from municipal solid waste incineration. Applied Catalysis B: Environmental 205, 310-318

Gallastegi-Villa M, Aranzabal A, González-Marcos MP, Markaide-Aiastui BA, González-Marcos JA, González-Velasco JR (2020): Effect of vanadia loading on acidic and redox properties of VO<sub>x</sub>/TiO<sub>2</sub> for the simultaneous abatement of PCDD/Fs and NO<sub>x</sub>. Journal of Industrial and Engineering Chemistry 81, 440-450

Gannoun C, Turki A, Kochkar H, Delaigle R, Eloy P, Ghorbel A, Gaigneaux EM (2014): Elaboration and characterization of sulfated and unsulfated V2O<sub>5</sub>/TiO<sub>2</sub> nanotubes catalysts for chlorobenzene total oxidation. Applied Catalysis B: Environmental 147, 58-64

James SL, Adams CJ, Bolm C, Braga D, Collier P, Friščić T, Grepioni F, Harris KDM, Hyett G, Jones W, Krebs A, Mack J, Maini L, Orpen AG, Parkin IP, Shearouse WC, Steed JW, Waddell DC (2012): Mechanochemistry: opportunities for new and cleaner synthesis. Chemical Society Reviews 41, 413-447

1. S. W. SING DHE, R. A. W. HAUL, L. MOSCOU, , R. A. PIEROTTI JR, T. SIEMIENIEWSKA (1985): Reporting physisorption data for gas/soild systems with Special Reference to the Determination of Surface Area and Porosity. Pure & Appl. Chem. 57, 603-619

Kang M, Park ED, Kim JM, Yie JE (2007): Manganese oxide catalysts for NO<sub>x</sub> reduction with NH<sub>3</sub> at low temperatures. Applied Catalysis A: General 327, 261-269

Kwon DW, Park KH, Hong SC (2013): The influence on SCR activity of the atomic structure of V2O<sub>5</sub>/TiO<sub>2</sub> catalysts prepared by a mechanochemical method. Applied Catalysis A: General 451, 227-235

McKay G (2002): Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. Chemical Engineering Journal 86, 343-368

Muñoz-Batista MJ, Rodriguez-Padron D, Puente-Santiago AR, Luque R (2018): Mechanochemistry: Toward Sustainable Design of Advanced Nanomaterials for Electrochemical Energy Storage and Catalytic Applications. *ACS Sustainable Chemistry & Engineering* 6, 9530-9544

Oh J-E, Gullett B, Ryan S, Touati A (2021): Chlorobenzenes, chlorophenols, PAHs and low chlorinated dioxin/furan as post-boiler toxicity indicators in municipal solid waste incinerators. *Organohalogen Compounds* 66: 777-782.

Ralphs K, Hardacre C, James SL (2013): Application of heterogeneous catalysts prepared by mechanochemical synthesis. *Chem Soc Rev* 42, 7701-18

Wang J, Wang X, Liu X, Zhu T, Guo Y, Qi H (2015): Catalytic oxidation of chlorinated benzenes over V2O5/TiO2 catalysts: The effects of chlorine substituents. *Catalysis Today* 241, 92-99

Wang Q, Hung PC, Lu S, Chang MB (2016): Catalytic decomposition of gaseous PCDD/Fs over V2O5/TiO2-CNTs catalyst: Effect of NO and NH3 addition. *Chemosphere* 159, 132-137

Wang Q, Tang M, Peng Y, Du C, Lu S (2018): Ozone assisted oxidation of gaseous PCDD/Fs over CNTs-containing composite catalysts at low temperature. *Chemosphere* 199, 502-509

Xujian Z, Xiaodong L, Xianhua M, Shasha J, Mingjiang N, Kefa C (2014): Adsorption of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans Vapors on Activated Carbon. *Environmental Engineering Science* 31, 664-670

Yang RT, Long RQ, Padin J, Takahashi A, Takahashi T (1999): Adsorbents for Dioxins: A New Technique for Sorbent Screening for Low-Volatile Organics. *Industrial & Engineering Chemistry Research* 38, 2726-2731

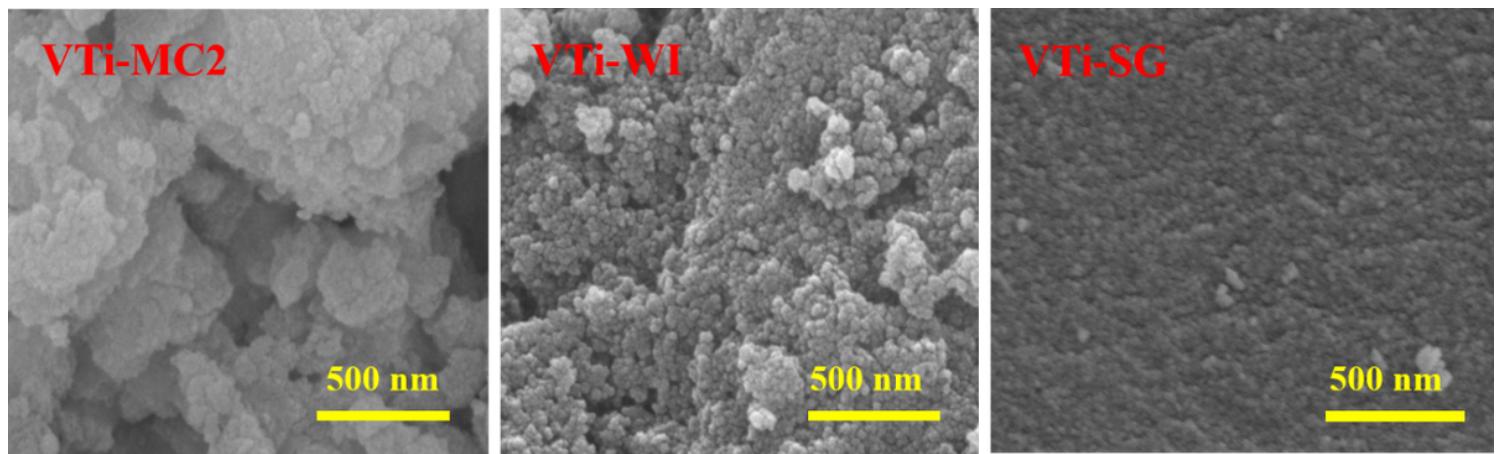
Yang Y, Zhang S, Wang S, Zhang K, Wang H, Huang J, Deng S, Wang B, Wang Y, Yu G (2015): Ball Milling Synthesized MnO<sub>x</sub> as Highly Active Catalyst for Gaseous POPs Removal: Significance of Mechanochemically Induced Oxygen Vacancies. *Environmental Science & Technology* 49, 4473-4480

Yu M-f, Lin X-q, Li X-d, Yan M, Prabowo B, Li W-w, Chen T, Yan J-h (2016): Catalytic destruction of PCDD/Fs over vanadium oxide-based catalysts. *Environmental Science and Pollution Research* 23, 16249-16258

Zhang S, Huang J, Yang Y, Li Y, Wang B, Wang Y, Deng S, Yu G (2015): Rapid mechanochemical synthesis of VO<sub>x</sub>/TiO<sub>2</sub> as highly active catalyst for HCB removal. *Chemosphere* 141, 197-204

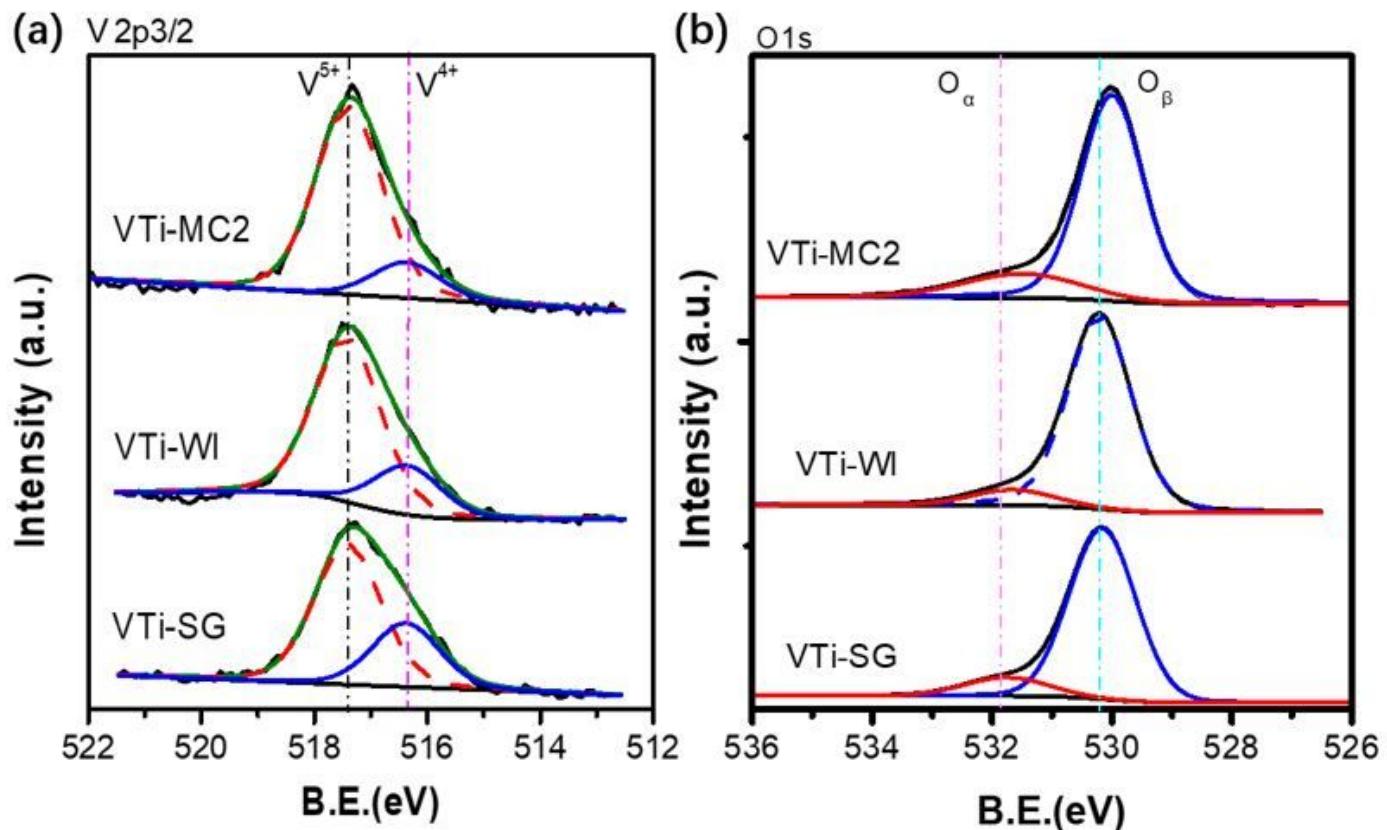
Zhao H, Bennici S, Shen J, Auroux A (2009): The influence of the preparation method on the structural, acidic and redox properties of V2O5-TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>-catalysts. *Applied Catalysis a-General* 356, 121-128

## Figures



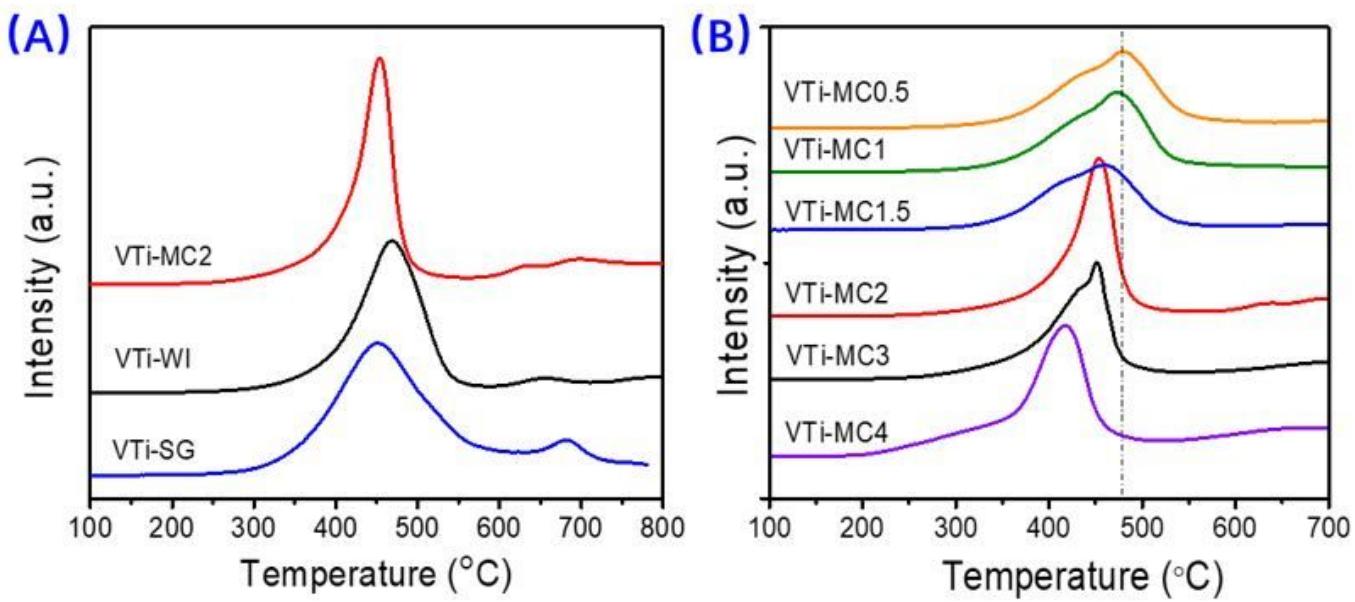
**Figure 1**

SEM images of various VO<sub>x</sub>/TiO<sub>2</sub> catalyst samples



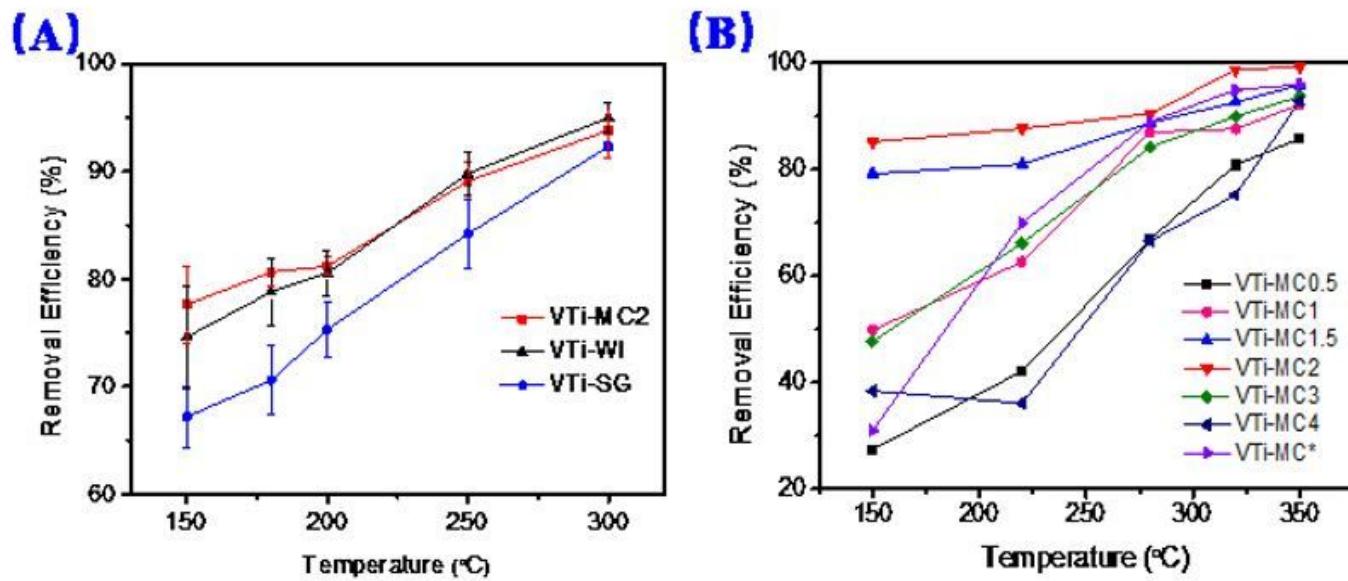
**Figure 2**

XPS patterns of various VO<sub>x</sub>/TiO<sub>2</sub> samples (a) V 2p 3/2, (b) O1s.



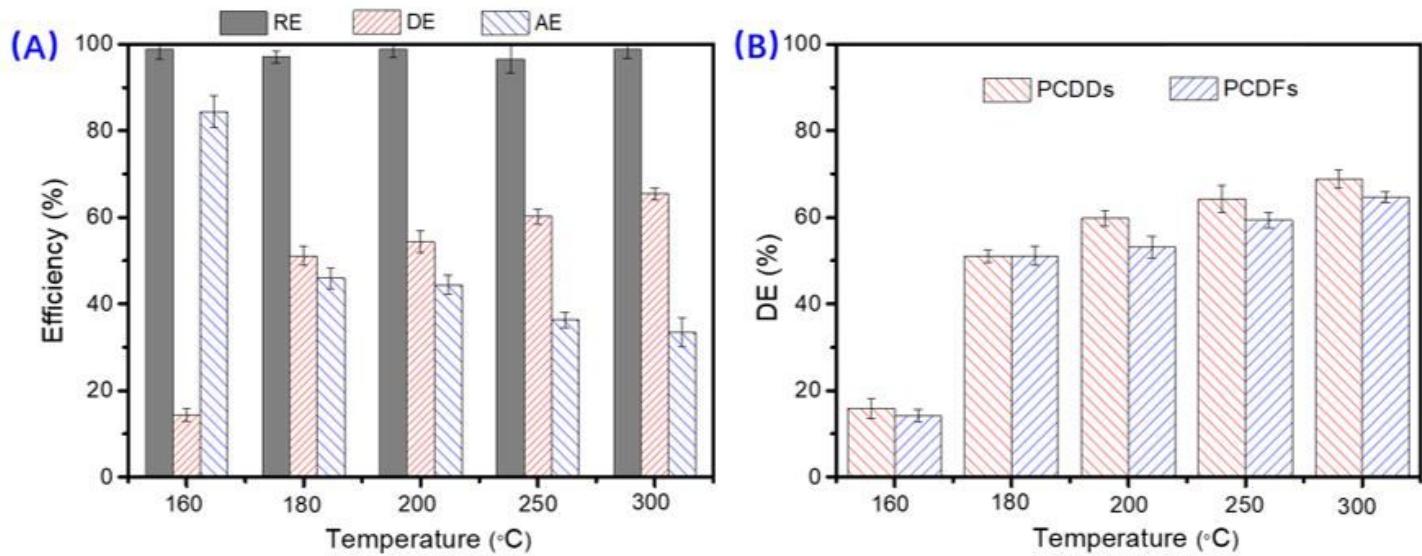
**Figure 3**

H<sub>2</sub>-TPR profiles of (A) various VO<sub>x</sub>/TiO<sub>2</sub> samples prepared by different methods, and (B) VTi-MC<sub>t</sub> catalysts.



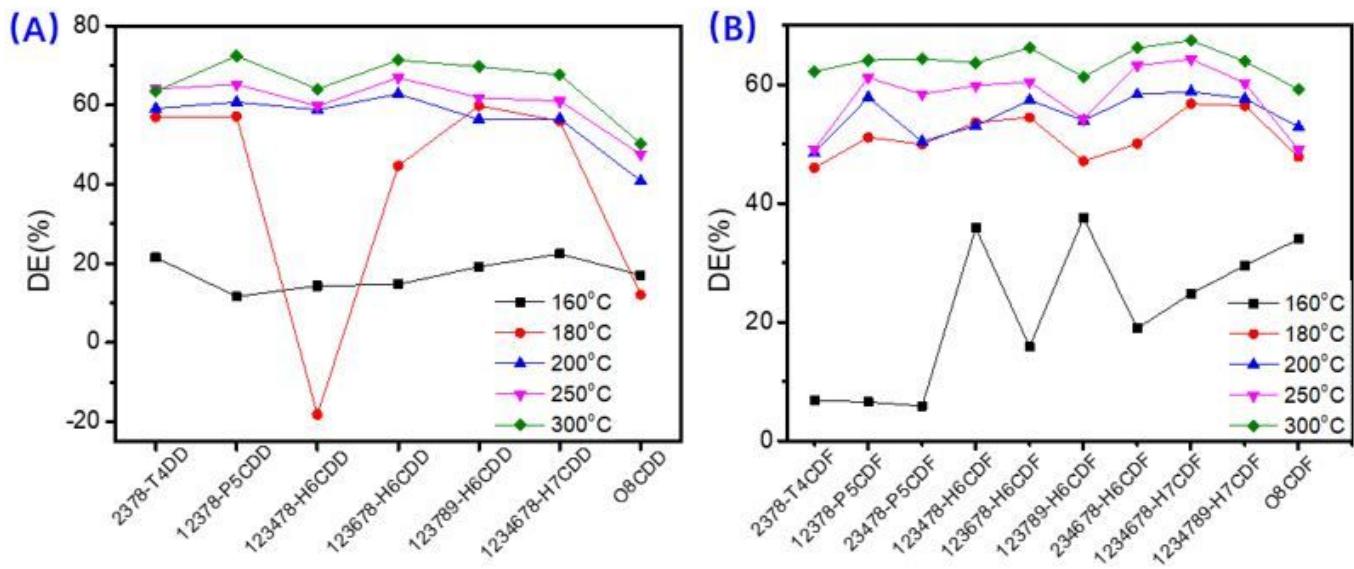
**Figure 4**

(A) The 1,2-DCBz removal efficiency of various VO<sub>x</sub>/TiO<sub>2</sub> samples (7000 h<sup>-1</sup>, 228 ppm); (B) The 1,2-DCBz removal efficiency of various VO<sub>x</sub>/TiO<sub>2</sub> samples with different Ball milling time and different precursor (7000 h<sup>-1</sup>, 117 ppm).



**Figure 5**

(A) The PCDD/Fs Removal Efficiency (RE), Degradation Efficiency (DE) and Adsorption Efficiency (AE) of VTi-MC2 at different temperature. (B) The total toxic equivalent degradation efficiency (DE) of PCDDs and PCDFs at different temperature. Reaction condition: SV= 20,000 h<sup>-1</sup>, inlet PCDD/Fs=3.20 ng TEQ/Nm<sup>3</sup>, 1h.



**Figure 6**

The degradation efficiency of 17 PCDD/Fs homologues at different temperature (SV= 20,000 h<sup>-1</sup>, inlet PCDD/Fs = 3.20 ng TEQ/Nm<sup>3</sup>, reaction time=1 h)

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