

CATALYTIC DESTRUCTION OF GASEOUS PCDD/Fs OVER MODIFIED V-TYPE CATALYST

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1. Introduction

Previous studies indicate that selective catalytic reduction (SCR) catalysts (TiO₂-based V₂O₅/WO₃) originally designed for the removal of nitrogen oxides (NO_x) are also effective in the decomposition of PCDD/Fs at same temperature as that used for the DeNO_x.^{1,2} The removal efficiency of SCR system achieved with TiO₂-based V₂O₅/WO₃ catalysts in 230°C for PCDD/Fs could even reach 98.2%.

So far, a variety of catalysts have been developed for PCDD/Fs removal. Generally, these catalysts can be classified into noble and transition metals based on the active metals applied. Among the noble metals, Pt, Pd, and Rh are commonly used. These catalysts can achieve as high as 90% removal efficiency at 300°C; however, relatively high cost has limited its application.^{3,4} Major transition metals being used as catalysts include VO_x, CrO_x, MnO_x, and FeO_x.^{5,6} V₂O₅ is of the highest activity while FeO_x is of the lowest activity toward PCDD/F decomposition. Mobil Central Research Laboratory (in early 1990s) discovered the mesoporous molecular sieves of the MCM-41 type.⁷ This material (MCM type) is characterized by a regular arrangement of uniform mesopores bridged the gap between zeolites and other amorphous forms of silica, due to pores size and their spatial distribution.⁸ Since then, a growing interest has manifested in testing these new materials as catalysts, catalyst-precursors or catalyst supports. Attempts to prepare vanadium-containing MCM-41 type solids were successful and the solids exhibiting interesting catalytic properties were obtained.^{9,10} Despite a relatively abundant literature concerning the application of modified MCM-41 as catalysts in the liquid phase, very few studies have been devoted to the removal of gas-phase pollutants such as NO_x and PCDD/Fs.

2. Materials and methods

2.1. Catalyst characterization

MCM-41 and V₂O₅/MCM-41(HM) mesoporous material was prepared with hydrothermal method (HM). A solution of CTMABr (hexdecyl-trimethylammonium bromide), which was prepared by dissolving CTMABr in deionized water, was added dropwise to the solution of Na-silicate in deionized water (V₂O₅/MCM-41(HM) had to add NH₄VO₃) under stirring at room temperature for 30 minutes. The pH value of the mixture was adjusted to 9.7 using 1.2 M of H₂SO₄ solution. After stirring continuously for additional 3 hours at room temperature, the mixture was transferred into a polypropylene bottle and statically heated at 105°C for 3 days. The resulting solid product was recovered by filtration, and washed with deionized water. The solids were then calcined in air at 560°C for 6 hours, using a heating rate of 5°C/min.

V₂O₅ catalysts are supported on 70% anatase-30% rutile TiO₂ (Degussa P25) and prepared by incipient wetness impregnation method. The precursors including NH₄VO₃ are dissolved in distilled water. The suspension of support in the impregnation solution was stirred and heated to form colloidal solid. The solids obtained were dried for 1h in an oven at 105°C and then calcined at 400°C at atmospheric pressure in air for 4 h in the furnace. V₂O₅/MCM-41(IWT) was prepared by incipient wetness impregnation (IWT) of MCM-41 mesoporous support with an aqueous solution of NH₄VO₃.

2.2 Dioxin-containing gas stream generating system

The experimental tests were carried out with a continuous gas flow system equipped with a dioxin-containing gas stream generating subsystem as shown in Fig. 1.

The effects of operating parameters including types of catalysts, operating temperature on the removal efficiencies of PCDD/Fs are investigated. The feeding gas is composed of 10% O₂ and the dioxin concentration is 15 ng-TEQ/Nm³. The total flow rate of the feed gas is 2 L/min that gives rise to the gas hourly space velocity (GHSV) of 20,000 h⁻¹. The operating temperature varies from 150 to 250°C.

PCDD/F sample was collected by XAD-2 and extracted with toluene. The sample was then subjected to a series of clean up columns including sulfuric acid silica gel column, acidic aluminum oxide column, and carbon column. The 17 target PCDD/F compounds are collected together and analyzed with HRGC/HRMS.

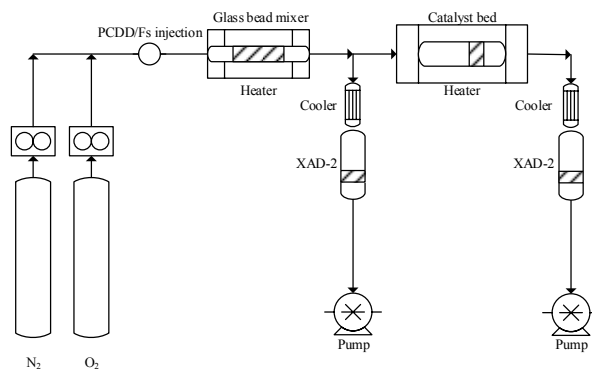


Fig. 1. Schematic diagram of the experimental system for evaluating PCDD/F removal.

3. Results and discussion

3.1 Characterization of the catalysts

Fig. 2(a) shows the X-ray powder diffraction patterns of the catalysts prepared. An intense diffraction peak (100) together with an additional peak (110) and a very weak peak (200), characteristics of hexagonal ordered MCM41 structure, were observed in the XRD patterns of the materials prepared.^{11,12,13} The XRD patterns of catalysts show a peak at the two theta degree of 2-2.5, while that prepared by hydrothermal method is weaker than that prepared with incipient wetness impregnation. This indicates that V₂O₅ may interfere with MCM-41 formation, resulting in the weak peak for the material synthesized by hydrothermal method. Fig. 2(b) indicates that TiO₂ (Degussa P25) has two crystal types including anatase and rutile. The BET specific surface area and elemental composition of the catalysts prepared are presented in Table 1. The major differences of catalysts are in terms of carrier and vanadium loadings, and specific surface areas of the catalyst with the carrier of TiO₂ is smaller than that of MCM-41.

The specific surface areas of 1% and 5% V₂O₅/MCM-41(HM) catalyst are 964.23 m²/g and 993.51 m²/g, respectively. The catalysts prepared by incipient wetness impregnation (1% and 5% V₂O₅/MCM-41(IWT)) are of smaller specific surface area than that prepared by hydrothermal method as indicated in Table 1. With incipient wetness impregnation, MCM-41 was prepared first and then coated with V₂O₅, causing the specific surface areas to decrease. MCM-41 possesses a uniform arrangement of hexagonally ordered pores of diameters ranging from 20 to 100 Å. The average pore diameters of the materials prepared by two synthetic methods are within this range.

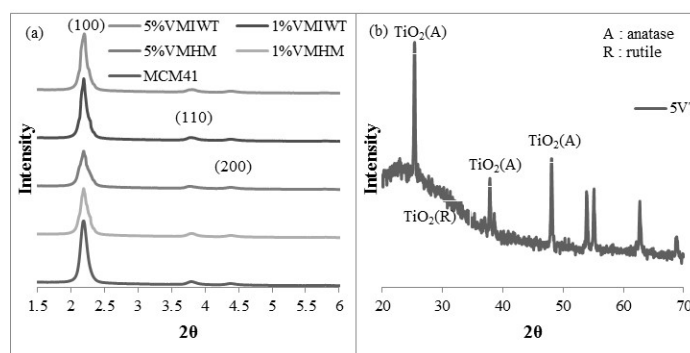


Fig. 2. XRD patterns of catalysts

Table 1 Characterization of the catalysts prepared

Catalyst	BET Surface Area (m ² /g)	EDS (wt%)			
		Si	V	O	Ti
5% V ₂ O ₅ /TiO ₂	53.4	-	5.9	10.6	83.5
1% V ₂ O ₅ /MCM-41(HM)	964.2	71.54	0.98	27.48	-
5% V ₂ O ₅ /MCM-41(HM)	993.5	68.84	4.92	26.24	-
1% V ₂ O ₅ /MCM-41(IWT)	784.8	65.33	1.33	33.34	-
5% V ₂ O ₅ /MCM-41(IWT)	737	63.58	5.09	31.33	-

3.2 Effect of gas temperature

Generally, the gas temperature is one of the most important factors affecting the removal efficiency. A series of experimental tests were carried out at different temperatures with the same inlet PCDD/F concentration of 15 ng TEQ Nm⁻³. Fig. 3 shows the PCDD/F removal efficiency, destruction efficiency and adsorption efficiency achieved with 5wt% V₂O₅/TiO₂ at different operating temperatures (150, 200, and 250°C). Fig. 4 shows that 5 wt% V₂O₅/TiO₂ has the highest PCDD/F removal efficiency, followed by V₂O₅/MCM-41(IWT). The experimental results indicate that the PCDD/Fs removal efficiency achieved with of 5wt% V₂O₅/TiO₂ reached 99.4% at 150°C, and as the temperature is increased to 200°C, the PCDD/F removal efficiency even reached 99.9%. It is attributed to the carrier of catalysts. TiO₂ (anatase) is considered as the best support of SCR catalysts because vanadium oxide can be uniformly dispersed to monolayer coverage on the surface of TiO₂.^{14,15}

For hydrothermal method, precursor of V₂O₅ and MCM41 are added at the same time, causing MCM41 to cover the active sites of V₂O₅ after synthesis process. MCM-41 is composed of silica (Table 1) which causes catalysis and adsorption to occur simultaneously. Fig.5. shows removal efficiencies of PCDD/Fs achieved with 5wt% V₂O₅/MCM-41 (HM) congener at 150°C. In general, the removal efficiencies of PCDD/F congeners decrease with increasing chlorination level. It is attributed to the fact that the highly chlorinated PCDD/F congeners are of more stable structures compared with the low chlorinated congeners, resulting in lower oxidation rates. However, the catalyst with MCM-41 as carrier shows opposite trend and the removal efficiency increases with increasing chlorination level. Since catalysis and adsorption occur simultaneously, more effective adsorption of highly chlorinated PCDD/F congeners results in the increase of removal efficiency with increasing chlorination level.

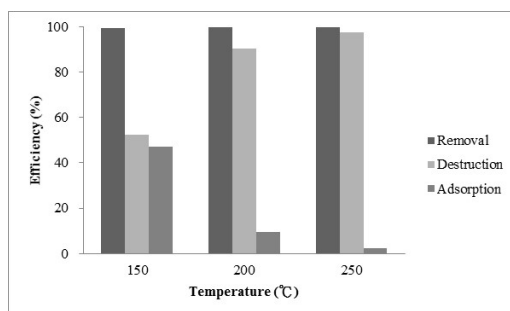


Fig. 3. Removal, destruction and adsorption efficiencies of PCDD/Fs achieved with 5wt% V₂O₅/TiO₂ at different operating temperatures.

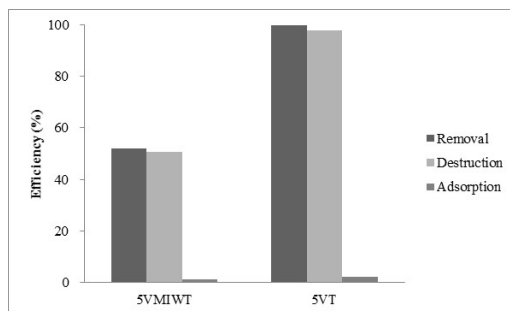


Fig. 4. Removal, destruction and adsorption efficiencies of PCDD/Fs achieved with 5 wt% V₂O₅/MCM-41(IWT) and 5wt% V₂O₅/TiO₂, respectively, at 250°C.

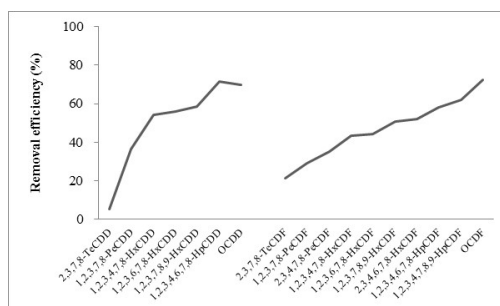


Fig. 5. Removal efficiencies of PCDD/F congeners achieved with 5wt% V₂O₅/MCM-41 (HM) at 150°C.

Acknowledgements

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