# **Electronic Supplementary Information**

# The Additives and Intermediates on Vanadia-Based Catalyst for Multi-Pollutants Control

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## 1. Experimental

#### 1.1 Catalysts preparation

The vanadia based catalysts in this paper were prepared by a traditional impregnation method same as our research group previous study.<sup>1</sup> Catalysts were support on a 100% anatase TiO<sub>2</sub> (Macklin). The active phase is V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub> and WO<sub>3</sub> introduced as dopes. The precursors of these oxides are respectively analytical grade NH<sub>4</sub>VO<sub>3</sub> (Sinopharm Chemical Reagent, 99.99%), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Sinopharm Chemical Reagent, 99.99%), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Sinopharm Chemical Reagent, 99.99%). The Mo/VTi catalyst was with V<sub>2</sub>O<sub>5</sub> content of 1% w/w and MoO<sub>3</sub> content of 5% w/w. The Mo-W/VTi catalyst was with V<sub>2</sub>O<sub>5</sub> content of 1% w/w, MoO<sub>3</sub> content of 1% w/w and WO<sub>3</sub> content of 1% w/w.

#### 1.2 Catalytic tests

Analysis of the reactants and products were performed on-line with GASMET FTIR DX-4000. The catalytic activity tests for all the catalysts were performed in a fixed-bed quartz reactor. 0.2 g granular catalyst (40–60 mesh) was used for each evaluation.

For single catalytic oxidation activity tests of chlorobenzene (CB), the feed gas stream contained 100 ppm of CB, 3%  $O_2$  and  $N_2$  as the balance. The total flow rate of the feed gas stream was 100 mL/min, the corresponding gas hourly space velocity (GHSV) was 30000 h<sup>-1</sup>. All the catalytic tests were run from 100 °C to 450 °C in a step mode. At each temperature tested, the catalyst was stabilized for 1 h to achieve steady

state.

For single SCR performance tests, the feed gas mixture contained 500 ppm NO, 500 ppm NH<sub>3</sub>, 3%  $O_2$  and  $N_2$  as the balance. The total flow rate of the feed gas stream was 100 mL/min, the corresponding gas hourly space velocity (GHSV) was 30000 h<sup>-1</sup>. All the catalytic tests were run from 100 °C to 450 °C in a step mode. At each temperature tested, the catalyst was stabilized for 1 h to achieve steady state.

For simultaneous removal activity tests of NO and CB, the feed gas mixture contained 500 ppm NO, 500 ppm NH<sub>3</sub>, 100 ppm CB, 3% O<sub>2</sub> and N<sub>2</sub> as the balance. The total flow rate of the feed gas stream was 100 mL/min, the corresponding gas hourly space velocity (GHSV) was 30000 h<sup>-1</sup>. All the catalytic tests were run from 100 °C to 450 °C in a step mode. At each temperature tested, the catalyst was stabilized for 1 h to achieve steady state.

The  $N_2$  of  $NH_3$ -SCR,  $CO_x$  and HCl selectivity of CBCO were calculated based on the following Eqs. (S1)–(S3):

$$N_{2} \text{ selectivity} = \begin{cases} 1 - \frac{2C^{out}N_{2}O}{C^{in}_{NO_{x}} + C^{in}_{NH_{3}} - C^{out}_{NO_{x}} - C^{out}_{NH_{3}}} \end{cases}$$
(S1)

$$CO_{x} \text{ selectivity} = \frac{C^{out}_{CO_{x}} - C^{in}_{CO_{x}}}{6(C^{in}CB - C^{out}CB)[\%]}$$
(S2)

HCl selectivity = 
$$\frac{C^{out}_{HCl} - C^{in}_{HCl}}{C^{in}CB - C^{out}CB[\%]}$$
(S3)

#### 1.3 Catalysts characterization

X-ray diffraction patterns (XRD) were recorded on RINT2000 vertical goniometer by using CuK $\alpha$  ( $\lambda$ =0.15405nm, 40 kV, 200 mA) with the 2 $\theta$  range from 10-90° at a step of 8°. Specific surface area and pore volume measurements of the catalysts were done by nitrogen physisorption at -196 °C on an adsorption unit (Quantachrome, Autosorb-1). Prior to the analysis, the catalysts were outgassed at 300 °C for 4 h.

Temperature programmed desorption (TPD) was carried out with GASMET FTIR DX-4000. The TPD tests for all the catalysts were performed in a fixed-bed quartz reactor. 0.1 g granular catalyst (40–60 mesh) was used for each evaluation.

NH<sub>3</sub>-TPD: The samples were first pretreated at 300 °C for 1 h in N<sub>2</sub> and then cooled down to 30 °C. After that, the samples were exposed to 500 ppm NH<sub>3</sub>/N<sub>2</sub> for 1 h at 30 °C until adsorption equilibrium, followed by N<sub>2</sub> purge for another 1 h at 30 °C. Finally, the TPD tests were run at the rate of 10 °C/min from 30 to 750 °C in 100mL/min N<sub>2</sub>.

CB-TPD: The samples were first pretreated at 300 °C for 1 h in N<sub>2</sub> and then cooled down to 30 °C. After that, the samples were exposed to 100 ppm CB/N<sub>2</sub> for 1 h at 30 °C until adsorption equilibrium, followed by N<sub>2</sub> purge for another 1 h at 30 °C. Finally, the TPD tests were run at the rate of 10 °C/min from 30 to 750 °C in 100mL/min N<sub>2</sub>.

NH<sub>3</sub>+CB-TPD: The samples were first pretreated at 300 °C for 1 h in N<sub>2</sub> and then

cooled down to 30 °C. After that, the samples were exposed to 500 ppm  $NH_3/N_2$  and 100 ppm  $CB/N_2$  for 1 h at 30 °C until adsorption equilibrium, followed by  $N_2$  purge for another 1 h at 30 °C. Finally, the TPD tests were run at the rate of 10 °C/min from 30 to 750 °C with 100mL/min  $N_2$ .

Surface deposition (SD)-TPD: The samples were first pretreated at 300 °C for 1 h in  $N_2$  and then cooled down to 30 °C. After that, the samples were having simultaneous removal reaction of NO and CB for 3 h at 325 °C, followed by  $N_2$  purge for another 1 h until cool down to 30 °C. Finally, the TPD tests were run at the rate of 10 °C/min from 30 to 750 °C in 100mL/min  $N_2$ .

Temperature programmed surface reaction (TPSR) was carried out with GASMET FTIR DX-4000. The TPSR tests for all the catalysts were performed in a fixed-bed quartz reactor. 0.1 g granular catalyst (40–60 mesh) was used for each evaluation. The samples were first pretreated at 300 °C for 1 h in N<sub>2</sub> and then cooled down to 30 °C. After that, the samples were exposed to 500 ppm NH<sub>3</sub>/N<sub>2</sub>, 500 ppm NO/N<sub>2</sub>, 100 ppm CB/N<sub>2</sub> and 3% O<sub>2</sub> for 1 h at 30 °C until adsorption equilibrium, followed by N<sub>2</sub> purge for another 1 h at 30 °C. Finally, the TPSR tests were run at the rate of 10 °C/min from 30 to 750 °C in 100mL/min 3% O<sub>2</sub>/N<sub>2</sub>.

TG-IR-MS tests were run by TG-IR-GC/MS triplex analyzer (PerkinElmer). 100 mg granular catalyst (40–60 mesh) was used for each evaluation. Helium was used as the carrier gas to carry the compounds desorbed from TG process to IR and MS units. The TG unit was run at the rate of 10 °C/min from 30 to 1000 °C. Samples were monitored online by MS in the scanning range of 45–300 (m/z).

The XRD patterns of the prepared catalysts are obtained in Fig. S1, and the only observed peaks can be attributed to the  $TiO_2$  anatase,  $V_2O_5$ ,  $MoO_3$  and  $WO_3$  are well dispersed on the supports. The general description of the catalysts is shown in Table S1.



Fig. S1. XRD patterns of the vanadia based catalysts.

	Mo/VTi	Mo-W/VTi	W/VTi
SA $(m^2g^{-1})$	63.53	62.88	58.78
$PV (cm^3g^{-1})$	0.31	0.31	0.31

Table S1. General description of the vanadia catalysts: specific surface, pore volume.



Fig. S2. SCR performance of: Mo/VTi, Mo-W/VTi, W/VTi catalysts with 5% H<sub>2</sub>O at 225 °C. Reaction conditions:  $[NH_3] = [NO] = 500$  ppm, [CB] = 100 ppm,  $[O_2] = 3\%$ , catalyst mass = 200 mg, total flow rate = 100 mL min<sup>-1</sup>, gas hourly space velocity (GHSV) = 30000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>.



Fig. S3. H<sub>2</sub>-TPR results of Mo/VTi, Mo-W/VTi and W/VTi catalysts in the range of 100-900 °C.

For Mo/VTi, two bands roughly at 400 °C and 750 °C were found. The peak at low temperature belongs to the reduction of  $V^{5+}$  to  $V^0$ ,  $Mo^{6+}$  to  $Mo^{3+}$ , while the band at high temperature belongs to the reduction of  $Mo^{3+}$  to  $Mo^0$ .

For W/VTi, two bands roughly at 450 °C and 800 °C were found. The peak at low temperature belongs to the reduction of  $V^{5+}$  to  $V^0$ ,  $W^{6+}$  to  $W^{4+}$ , while the band at high temperature belongs to the reduction of  $W^{4+}$  to  $W^0$ .

Compared with the reduction peaks of W/VTi, the two reduction peaks of Mo/VTi were located at lower temperatures.



Fig. S4. TPD results of Mo/VTi catalyst.



Fig. S5. The CO, CO<sub>2</sub> and HCl selectivity results of Mo/VTi catalyst with/without the presence of SCR reactants in the reaction atmosphere.



Fig. S6. IR spectra of CBCO decomposition products over Mo/VTi catalyst without (a)/with (b) the presence of SCR reactants below 350°C.



Fig. S7. IR spectra of CBCO decomposition products over Mo/VTi catalyst without (a)/with (b) the presence of SCR reactants above 350°C.



Fig. S8. TPD results of  $NH_4Cl$  deposited Mo/VTi catalyst.

The pretreatment of NH<sub>4</sub>Cl deposited Mo/VTi catalyst:

the NH<sub>4</sub>Cl deposited Mo/VTi catalysts were prepared by impregnation of 2 g fresh Mo/VTi catalyst with 50 ml of 0.4 mol/L aqueous solution of NH<sub>4</sub>Cl, stirred at 60 °C by a magnetic stirring apparatus until excess water was evaporated, followed by drying in air at 60 °C for 12 h.



Fig. S9. a) SD-TPD results of Mo/VTi catalyst with  $N_2$  as carrier gas, b) SD-TPD results of W/VTi catalyst with  $N_2$  as carrier gas, c) SD-TPD results of Mo/VTi catalyst with 20%  $O_2$  in the carrier gas, d) SD-TPD results of W/VTi catalyst with 20%  $O_2$  in the carrier gas.

The SD-TPD results of Mo/VTi and W/VTi catalysts with N<sub>2</sub> as carrier gas are shown in Fig. S9a–b. For W/VTi, the desorption peak of HCl was not even detected, and the desorption peak of NH<sub>3</sub> was large and wide. Therefore, it can confirm that NH<sub>4</sub>Cl was not deposited at both catalysts' surface at 325 °C. And the desorption peak of NH<sub>3</sub> was originated from the NH<sub>3</sub> species that adsorbed at both catalysts' surface. Meanwhile, it's worth noticed that the amount of NH<sub>3</sub> desorbed form the surface of W/VTi was significantly higher than the amount of NH<sub>3</sub> desorbed form the surface of Mo/VTi. The SD-TPD results of Mo/VTi and W/VTi catalysts with 20% O<sub>2</sub> in the carrier gas are shown in Fig. S9c–d. As shown in Fig. S9c, the HCl was generated at relatively low temperature with a higher amount, compare to Fig. S9a. The desorption peak of HCl started to appeared at about 470 °C, reached the top at about 570 °C. As shown in Fig. S9d, the desorption peak of HCl started to appeared at about 590 °C, reached the top at about 650 °C. For both catalysts, the desorption of the deposited Cl species was promoted with the presence of  $O_2$ .

Carbon tetrachloride



Fig. S10. The IR spectrum of gas phase  $\text{CCl}_4$  from NIST database.  $^4$ 

Ethylene, tetrachloro-



Fig. S11. The IR spectrum of gas phase  $C_2 Cl_4$  from NIST database.  $^5$ 



Fig. S12. TG results of Mo/VTi catalyst after three hours reaction at 325 °C.



Fig. S13. XPS spectra of V 2p over fresh (a) and used (b) Mo/VTi catalysts.

Table S2. Vanadium valence distribution and Cl surface atomic ratio in Mo/VTi

Catalyst	V <sup>3+</sup> /V(%)	V <sup>4+</sup> /V(%)	V <sup>5+</sup> /V(%)
Mo/VTi-fresh	31.81	50.90	17.24
Mo/VTi-used 3h	45.62	45.13	9.25

samples obtained from XPS.

## 2. Computational details

Vienna Ab-initio Simulation Package code (VASP 5.2)<sup>2</sup> was applied for carrying out DFT computations. A  $2 \times 2 \times 1$  Mo/VTi supercell and a  $2 \times 2 \times 1$  W/VTi supercell were built respectively. We optimized these supercells with Perdew-Burke-Ernzerh of generalized gradient approximation (GGA-PBE).<sup>3</sup> The plane-wave cutoff energy was set to be 400 eV. Brillouin-zone integration was sampled by  $2 \times 2 \times 1$  k-points.

## References

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