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Electronic Supplementary Information

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Key intermediates from simultaneous removal of NO$_x$ and

chlorobenzene over a V$_2$O$_5$−WO$_3$/TiO$_2$ catalyst: a combined

experimental and DFT study

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Contents

25 ***1. The catalytic activity measurement***

26 The catalytic performance of $V_2O_5-WO_3/TiO_2$ was evaluated in a fixed-bed quartz

27 reactor. 200 mg of catalyst was used in simulated flue gas ([NO] = 500 ppm, [NH$_3$] =

28 500 ppm, [CB] = 50 ppm, [O$_2$] = 10 vol %, and N$_2$ as balance gas) with a gas hourly

29 space velocity (GHSV) of 60000 mL/(g·h). The conversion of NO$_x$ and CB, and the

30 selectivity of N$_2$, CO$_2$, and HCl were evaluated by the following equations:

31
$$\text{NO}_x \text{ conversion} = \frac{C_{\text{NO}_x}^{in} - C_{\text{NO}_x}^{out}}{C_{\text{NO}_x}^{in}} \times 100\% \tag{1}$$

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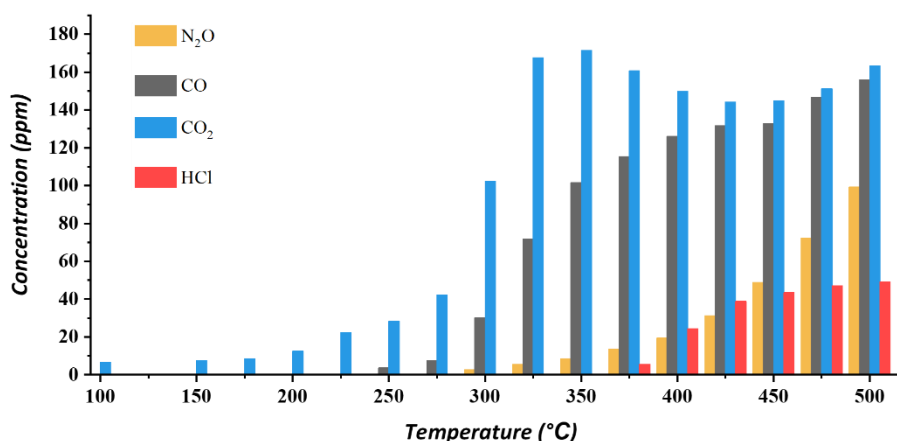$$\text{CB conversion} = \frac{C_{\text{CB}}^{in} - C_{\text{CB}}^{out}}{C_{\text{CB}}^{in}} \times 100\% \tag{2}$$

33
$$\text{N}_2 \text{ selectivity} = \left[1 - \frac{2C_{\text{N}_2\text{O}}^{out}}{C_{\text{NO}_x}^{in} + C_{\text{NH}_3}^{in} - C_{\text{NO}_x}^{out} - C_{\text{NH}_3}^{out}}\right] \times 100\% \tag{3}$$

34
$$\text{CO}_2 \text{ selectivity} = \frac{C_{\text{CO}_2}^{out}}{6 \times (C_{\text{CB}}^{in} - C_{\text{CB}}^{out})} \times 100\% \tag{4}$$

35
$$\text{HCl selectivity} = \frac{C_{\text{HCl}}^{out}}{C_{\text{CB}}^{in} - C_{\text{CB}}^{out}} \times 100\% \tag{5}$$

36 where *in* and *out* represented the NO$_x$ concentrations of the inlet and outlet.

37

Fig. S1. N_2O, CO, CO_2, and HCl concentrations during measurement. Reaction conditions: NO 500 ppm, NH_3 500 ppm, CB 50 ppm, O_2 10 vol %, N_2 as balance gas, GHSV 60000 mL/(g·h).

The first increment at 200 – 250 °C could be assigned to the total effect of sectional CB oxidation and CO_2 physical desorption. The CO_2 physical desorption was also observed below 200 °C because CB conversion was zero but we could detect a trace of CO_2. A sharp drop of CO_2 selectivity between 250 and 275 °C could be attributed to the completion of CO_2 desorption (**Fig. 1**). CO was formed in competition with CO_2, causing the decline of CO_2 selectivity. The second increment at 400 – 500 °C could be due to the occurrence of Water-Gas Shift reaction converting CO to CO_2 which kept the concentration of CO_2 and CO in balance.
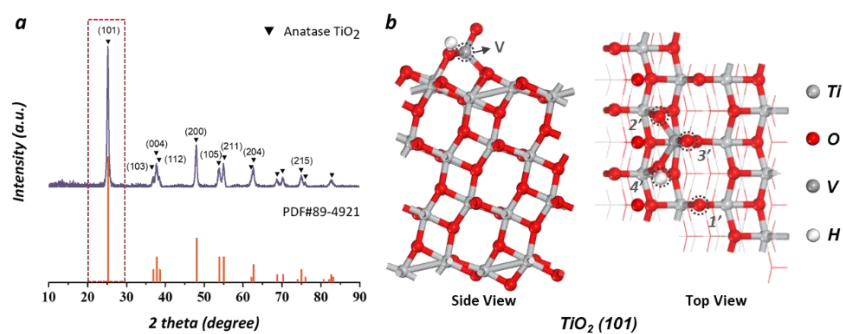
Fig. S2. XRD diffractograms of catalyst (a) and the optimized structure of catalyst (b).

The characteristic peaks at 25.3°, 37.0°, 37.8°, 38.6°, 48.1°, 53.9°, 55.1°, 62.8°, and 75.2° demonstrated that the catalyst structure was anatase TiO_2 phase (PDF#89-4921). No distinct characteristic peaks of vanadium oxides were detected, implying that these oxides were highly dispersed on TiO_2 support. The characteristic peak at 25.3° was attributed to (101) plane of anatase TiO_2 phase. Herein, a slab model of anatase TiO_2(101) surface was selected in this calculation. The V atom was fixed on the surface by three coordinated O atoms and H atom was bonded to O atom of V-O-Ti to form bridge hydroxyl structure according to previous work. The optimized structure was shown in **Figure S2 b** and four sites were considered in which *1', 2', 3',* and *4'* represented Ti-O-Ti, V-O-Ti, V=O, and V-O(H)-Ti, respectively.
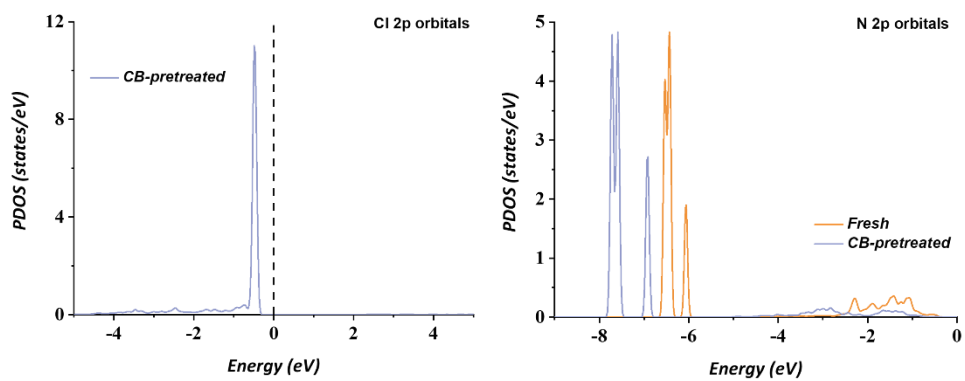
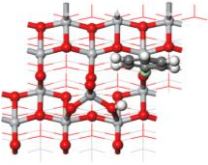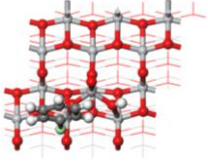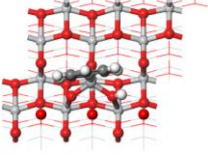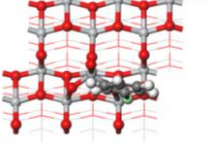65 **Fig. S3**. PDOS of Cl 2p and N 2p (NH_3) of the fresh catalyst and CB-pretreated catalyst.

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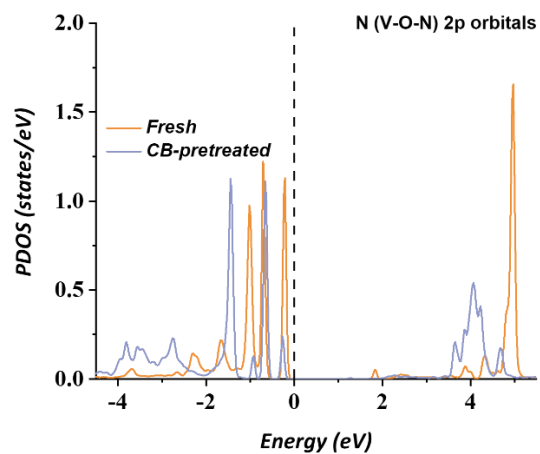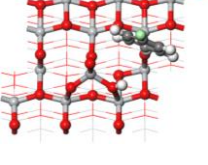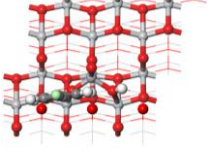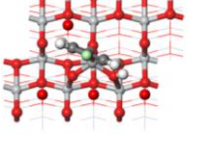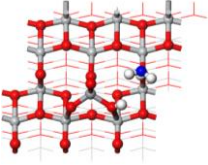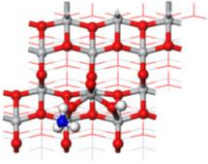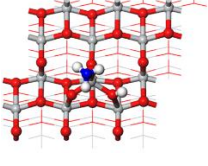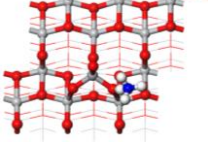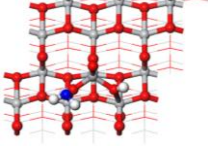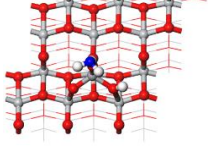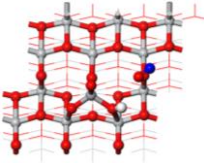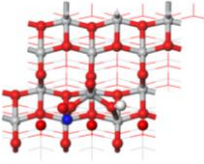
Fig. S4. PDOS of N 2p (cis-$N_2O_2^{2-}$) of the fresh catalyst and CB-pretreated catalyst.

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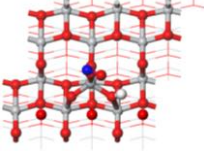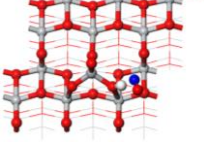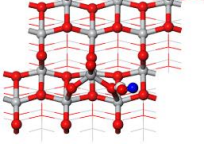**Table S1.** The adsorption energy (E_{ads}) of CB, NH_3, and NO.

Site [a]	Cl-1'	Cl-2'	Cl-3'	Cl-4'	H-1'	H-2'	H-3'
E_{ads} of CB (eV)	-0.1027	0.0018	-0.0047	-0.0876	-0.0576	-0.0158	-0.043
Optimized Structure							

Site	N-1'	N-2'	N-3'	N-4'	H-2'	H-3'
E_{ads} of NH_3 (eV)	-0.0913	-0.0217	0.0159	-0.7059	-0.0217	-0.0319
Optimized Structure						

Site	N-1'	N-2'	N-3'	N-4'	O-4'
E_{ads} of NO (eV)	-0.4193	-0.4515	-0.4391	-0.5121	-0.4231
Optimized Structure					

a represented the way of molecules adsorption on surface. For example, *Cl-1'* represented CB adsorbing on 3' site by Cl atom and its E_{ads} is -0.1027 eV.

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