Electronic Supporting Information:

Molybdenum-decorated V_2O_5-WO_3/TiO_2: Surface engineering toward boosting the acid cycle and redox cycle of NH_3-SCR

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Characterization

XRD patterns of the samples were obtained with a Bruker D8 Advance X-ray diffractometer with scan rate of 5°/min in the range from 20° to 80°. The BET method was used to measure the specific surface areas of the catalysts. The morphology of the catalyst was observed by SEM with a Hitachi SU8020. A FEI Tecnai G20 instrument was used to collect TEM and HRTEM images at an accelerating voltage of 200 kV. XPS experiments were performed with a Thermo Scientific Escalab 250Xi electron spectrometer, calibrated by the C 1 s peak at a binding energy (B.E.) of 284.6 eV. ICP data were collected by an iCAPQ6300 (Thermo Fisher). Raman experiments were carried out on a HORIBA HR Evolution spectrometer equipped with an optical microscope at room temperature. Dehydrated-Raman spectra were recorded at 250 °C in a feed gas of O2/He (5 vol.%H2/N2) with a flow rate of 60 mL/min after dehydration pretreatment at 400 °C for 0.5 h. 51V NMR experiments were performed on a Bruker AVANCE III 600 spectrometer operating at a frequency of 157.8 MHz. Spectra were obtained from 35000 scans with a 0.3 s recycle delay in a spectral width of 1 MHz.

H2-TPR and NH3-TPD were conducted on a Quantachrome AutoSorb IQ-C-TCD-MS analyzer and Micromeritics Autochem 2920, respectively. For H2-TPR, the sample (100 mg) was pretreated with a flow of He for 30 min at 300 °C. After cooling to room temperature, the sample was heated with a ramp of 10 °C/min in flowing H2 (5 vol.% H2/N2) with a flow rate of 50 mL/min. The temperature was increased from 30 °C to 1000 °C. For NH3-TPD, the sample (100 mg) was pretreated for 30 min at 300 °C in a flow of highly purified He. After cooling to room temperature, the sample was exposed to NH3 (1 vol% NH3/He) with a flow rate of 100 mL/min for 1 h at 30 °C, followed by purging with pure He to remove gaseous NH3 and physically adsorbed NH3. Finally, NH3 desorption took place in a 100 mL/min flow of He with heating rate of 10 °C/min from 30 °C to 800 °C.

In situ DRIFTs spectra were collected on a Nicolet 6700 FTIR spectrometer equipped with a high-temperature reaction cell. Before each test, the catalyst was pretreated in flowing N2 for 30 min at 400 °C. Subsequently, the temperature was cooled to 250 °C, and background spectra subtracted from the sample spectrum was recorded for each measurement. All spectra were recorded by accumulating 64 scans at a 4 cm⁻¹ resolution.
Catalytic Evaluation

The NH\textsubscript{3}-SCR activity was analyzed with a continuous fixed-bed quartz reactor (i.d. = 6 mm) at atmospheric pressure. The program temperature ranged from 100 °C to 400 °C. In each test, the catalyst was sieved to 40-60 mesh first, and then 0.5 g of sample was fixed on quartz wool in the middle of the reactor. Gaseous N\textsubscript{2} was used as the carrier gas, and the feed gas contained NO (600 ppm), NH\textsubscript{3} (600 ppm), O\textsubscript{2} (6.0 vol.%), SO\textsubscript{2} (100 ppm when used) and H\textsubscript{2}O (5.5% when used). The gas hourly space velocity (GHSV) was 51000 h\textsuperscript{−1} and the total flow rate was 600 mL/min. The concentrations of NO, NO\textsubscript{2}, N\textsubscript{2}O and NH\textsubscript{3} at the inlet and outlet were measured by a gas analyzer (Testo 350, Germany). The calculation equations of NO conversion and N\textsubscript{2} selectivity are as follows:

\[
\text{NO conversion} (\%) = (1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}) \times 100\% \tag{1}
\]

\[
\text{N}_2 \text{ selectivity} (\%) = (1 - \frac{[\text{NO}]_{\text{out}} + 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NH}_3]_{\text{out}}}) \times 100\% \tag{2}
\]

Assuming that the plug flow reactor (on the fixed catalyst bed) had no diffusion limitation, the NH\textsubscript{3}-SCR reaction rate coefficient (k) over the samples was calculated by the following equation:

\[
k = (-\frac{F_0}{[\text{NO}]_{\text{in}} W}) \times \ln(1 - x) \tag{3}
\]

where \(F_0\) represents the molar NO feed rate (mol/s), \([\text{NO}]_0\) represents the inlet NO molar concentration (mol/mL), \(W_{\text{cat}}\) represents the weight of sample (g), and \(x\) represents NO conversion (%).

The number of atoms per unit area was calculated as follows:\textsuperscript{[S1]}

\[
N_{\text{number}} = \frac{W N_A}{M A_{\text{BET}}} \tag{4}
\]

where \(N_{\text{number}}\) stands for the atom number of the element per unit area, \(W\) stands for the percentage of the element, \(N_A\) represents Avogadro’s constant, \(M\) represents relative the atomic mass of the element, and \(A_{\text{BET}}\) represents the BET specific surface area.
Table

**Table S1** Surface/bulk atomic concentration of the VW/Ti and xMo-VW/Ti (x=1, 3, 5, 7, and 9 wt.%) catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>bulk atomic concentration (wt.%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Surface atomic concentration (wt.%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>The ratio of bulk atomic to surface atomic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V</td>
<td>Mo</td>
<td>V</td>
</tr>
<tr>
<td>VW/Ti</td>
<td>0.717</td>
<td>0.491</td>
<td>0.69</td>
</tr>
<tr>
<td>1Mo-VW/Ti</td>
<td>0.712</td>
<td>1.06</td>
<td>0.502</td>
</tr>
<tr>
<td>3Mo-VW/Ti</td>
<td>0.706</td>
<td>2.99</td>
<td>0.534</td>
</tr>
<tr>
<td>5Mo-VW/Ti</td>
<td>0.686</td>
<td>5.23</td>
<td>0.601</td>
</tr>
<tr>
<td>7Mo-VW/Ti</td>
<td>0.670</td>
<td>7.37</td>
<td>0.648</td>
</tr>
<tr>
<td>9Mo-VW/Ti</td>
<td>0.690</td>
<td>10.6</td>
<td>0.480</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated by the ICP results.

<sup>b</sup>Calculated by the XPS results.
Table S2 The XPS results of the VW/Ti and xMo-VW/Ti (x=1, 3, 5, 7, and 9 wt.%) catalysts for O 1s, V 2p, Mo 3d, W 4f.

<table>
<thead>
<tr>
<th>Materials</th>
<th>O 1s BE (eV)</th>
<th>O$<em>{\text{latt}}$/O$</em>{\text{ads}}$(O$<em>{\text{latt}}$+O$</em>{\text{ads}}$)%</th>
<th>V 2p BE (eV)</th>
<th>V$^{4+}$/V$^{5+}$/V$^{5+}$/V$^{6+}$%</th>
<th>Mo 3d BE (eV)</th>
<th>Mo$^{5+}$/Mo$^{6+}$/Mo$^{6+}$/Mo$^{5+}$%</th>
<th>W 4f BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VW/Ti</td>
<td>530.2</td>
<td>531.4</td>
<td>28.0</td>
<td>516.2</td>
<td>517.2</td>
<td>67.2</td>
<td>-</td>
</tr>
<tr>
<td>1Mo-VW/Ti</td>
<td>530.2</td>
<td>531.2</td>
<td>28.5</td>
<td>516.3</td>
<td>517.4</td>
<td>68.2</td>
<td>231.5</td>
</tr>
<tr>
<td>3Mo-VW/Ti</td>
<td>530.2</td>
<td>531.1</td>
<td>28.6</td>
<td>516.3</td>
<td>517.4</td>
<td>70.4</td>
<td>231.8</td>
</tr>
<tr>
<td>5Mo-VW/Ti</td>
<td>530.2</td>
<td>531.1</td>
<td>29.1</td>
<td>516.3</td>
<td>517.5</td>
<td>71.8</td>
<td>232.0</td>
</tr>
<tr>
<td>7Mo-VW/Ti</td>
<td>530.1</td>
<td>531.1</td>
<td>29.5</td>
<td>516.4</td>
<td>517.5</td>
<td>73.3</td>
<td>232.1</td>
</tr>
<tr>
<td>9Mo-VW/Ti</td>
<td>530.1</td>
<td>531.1</td>
<td>25.1</td>
<td>516.4</td>
<td>517.5</td>
<td>71.2</td>
<td>232.3</td>
</tr>
</tbody>
</table>


Figures

**Fig. S1.** N$_2$O formation for the NH$_3$-SCR activity of the VW/Ti and xMo-VW/Ti (x=1, 3, 5, 7, and 9 wt.%) catalysts.
Fig. S2. (a-e) SEM images, and (f) EDX result of the 7Mo-VW/Ti catalyst.
Raman spectra of all catalysts at different ranges are depicted in Fig. S3. In Fig. S3a, the peaks at 147 cm$^{-1}$, 394 cm$^{-1}$, 514 cm$^{-1}$ and 636 cm$^{-1}$ were attributed to anatase TiO$_2$[S2,S3]. Raman spectra with a narrowed high scan range of 700-1200 cm$^{-1}$ are presented in Fig. S3b. The band at ~800 cm$^{-1}$ was ascribed to Ti-O vibration of TiO$_2$ or W=O stretching mode of crystalline WO$_3$[S4-S6]. According to a previous report,[S7] the doubly coordinated oxygen O-Mo-O stretching of the broadened asymmetric band centered at approximately 819 cm$^{-1}$ was not detected. The reasonable explanation was that little MoO$_3$ incorporated into the bulk phase, resulting in the formation of bulk-like MoO$_3$.[S8,S9] The band at 983 cm$^{-1}$ was attributed to terminal Mo=O stretching.[S10] It is obvious that the strength of the band at 970-980 cm$^{-1}$ increased and the shift occurred, indicating more polymeric molybdenum oxide formed.[S1,S10] When the loading amount of MoO$_3$ exceeded 7 wt.%., a weak peak of nearly 1000 cm$^{-1}$ appeared attributed to monomeric surface vanadia or a few crystalline MoO$_3$ species.[S11]
Fig. S4. XPS spectra for (a) W 4f and (b) Ti 2p of the VW/Ti and xMo-VW/Ti (x=1, 3, 5, 7, and 9 wt.%) catalysts.
Fig. S5. In situ DRIFTs spectra of the (a) 7Mo-VW/Ti and (c) VW/Ti catalysts pretreated by exposure to 600 ppm NO + 6 vol.% O₂ followed by exposure to 600 ppm NH₃ at 250 °C, and the corresponding mapping of the (b) 7Mo-VW/Ti, and (d) VW/Ti catalysts.

Fig. S5 shows the in situ DRIFTs spectra of the reaction between pre-adsorbed NO species and gaseous NH₃ on the 7Mo-VW/Ti and VW/Ti catalysts. The changes in the profiles on both of the 7Mo-VW/Ti and VW/Ti catalyst were very similar. After NO + O₂ pretreated and N₂ purging, no obvious peaks remained on both of the catalyst surface, suggesting that the capacity of NO adsorbed on the catalyst surface was very weak. As time went on for 5 min, a large amount of NH₄⁺(B) (1670 and 1423 cm⁻¹) and NH₃(L) (3380, 3356, 3161, 1244, and 1217 cm⁻¹) species were generated. The weak bands of NH₂ amide groups (1560 and 1327 cm⁻¹) from the intermediate of ammonia oxidation were also observed. In addition, for the 7Mo-VW/Ti catalyst, molybdenyl species acted as the adsorption sites for NH₃ adsorption, so a negative peak of Mo=O bond (1973 cm⁻¹) was found because of the influence of NH₃ to unsaturated molybdenyl species.
References


