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 O_2/He (5 vol.%H_2/N_2) with a flow rate of 60 mL/min after dehydration pretreatment at 400 °C for 0.5 h. ^{51}V 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.

H_2-TPR and NH_3-TPD were conducted on a Quantachrome AutoSorb IQ-C-TCD-MS analyzer and Micromeritics Autochem 2920, respectively. For H_2-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 H_2 (5 vol.% H_2/N_2) with a flow rate of 50 mL/min. The temperature was increased from 30 °C to 1000 °C. For NH_3-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 NH_3 (1 vol% NH_3/He) with a flow rate of 100 mL/min for 1 h at 30 °C, followed by purging with pure He to remove gaseous NH_3 and physically adsorbed NH_3. Finally, NH_3 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 N_2 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_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_2 was used as the carrier gas, and the feed gas contained NO (600 ppm), NH_3 (600 ppm), O_2 (6.0 vol.%), SO_2 (100 ppm when used) and H_2O (5.5% when used). The gas hourly space velocity (GHSV) was 51000 h^{-1} and the total flow rate was 600 mL/min. The concentrations of NO, NO_2, N_2O and NH_3 at the inlet and outlet were measured by a gas analyzer (Testo 350, Germany). The calculation equations of NO conversion and N_2 selectivity are as follows:

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

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

Assuming that the plug flow reactor (on the fixed catalyst bed) had no diffusion limitation, the NH_3-SCR reaction rate coefficient (k) over the samples was calculated by the following equation:

$$\text{k} = (-\frac{F_0}{[NO]_0 W}) \times \ln(1 - \text{x}) \quad (3)$$

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

The number of atoms per unit area was calculated as follows.[S1]

$$N_{number} = \frac{WN_A}{MA_{BET}} \quad (4)$$

where N_{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_{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.

Sample	bulk atomic concentration (wt.%)[a]		Surface atomic concentration (wt.%)[b]		The ratio of bulk atomic to surface atomic
	V	Mo	V	Mo	surface V/ bulk V
VW/Ti	0.717		0.491		0.69
1Mo-VW/Ti	0.712	1.06	0.502	1.87	0.71
3Mo-VW/Ti	0.706	2.99	0.534	2.07	0.76
5Mo-VW/Ti	0.686	5.23	0.601	3.23	0.88
7Mo-VW/Ti	0.670	7.37	0.648	5.65	0.97
9Mo-VW/Ti	0.690	10.6	0.480	6.96	0.70

[a]Calculated by the ICP results.

[b]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.

Materials	O 1s BE (eV)		$O_{ads}/(O_{ads}+O_{latt})$%	V 2p BE (eV)		$V^{4+}/(V^{4+}+V^{5+})$%	Mo 3d BE (eV)		$Mo^{6+}/(Mo^{6+}+Mo^{5+})$%	W 4f BE (eV)	
	O_{latt}	O_{ads}		V^{4+}	V^{5+}		Mo^{5+}	Mo^{6+}		W^{5+}	W^{6+}
VW/Ti	530.2	531.4	28.0	516.2	517.2	67.2	-	-	-	35.6	36.9
1Mo-VW/Ti	530.2	531.2	28.5	516.3	517.4	68.2	231.5	232.8	73.7	35.5	36.9
3Mo-VW/Ti	530.2	531.1	28.6	516.3	517.4	70.4	231.8	232.8	74.7	35.5	36.9
5Mo-VW/Ti	530.2	531.1	29.1	516.3	517.5	71.8	232.0	232.9	75.1	35.5	36.9
7Mo-VW/Ti	530.1	531.1	29.5	516.4	517.5	73.3	232.1	232.9	80.2	35.4	36.8
9Mo-VW/Ti	530.1	531.1	25.1	516.4	517.5	71.2	232.3	232.9	77.9	35.3	36.8

Figures

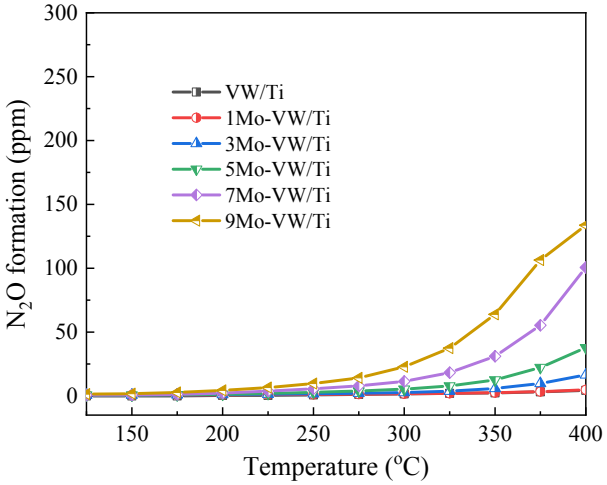

Fig. S1. N_2O formation for the NH_3-SCR activity of the VW/Ti and xMo-VW/Ti (x=1, 3, 5, 7, and 9 wt.%) catalysts.

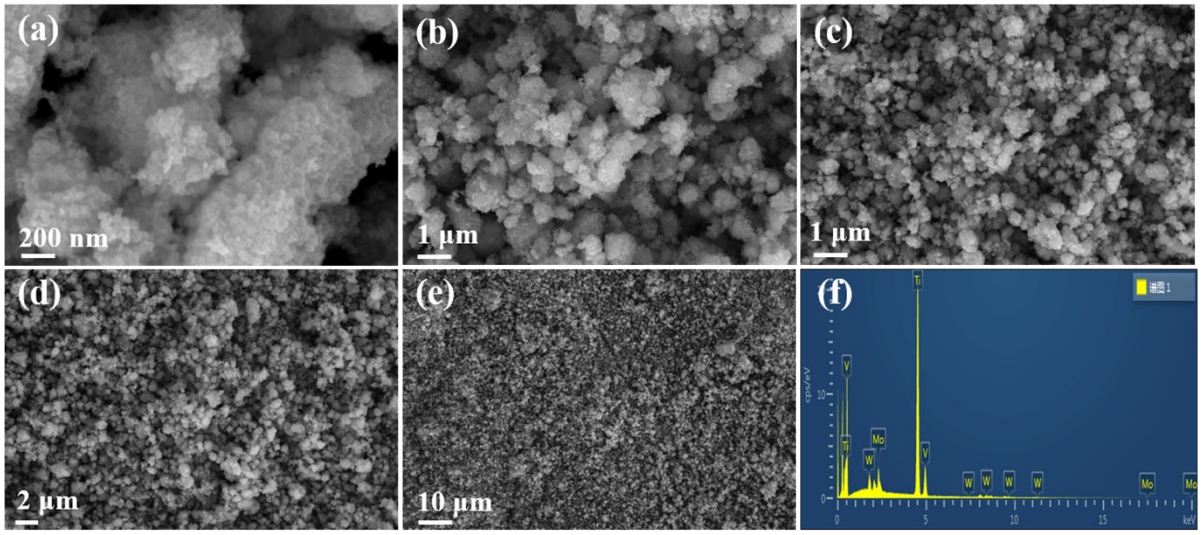

Fig. S2. (a-e) SEM images, and (f) EDX result of the 7Mo-VW/Ti catalyst.

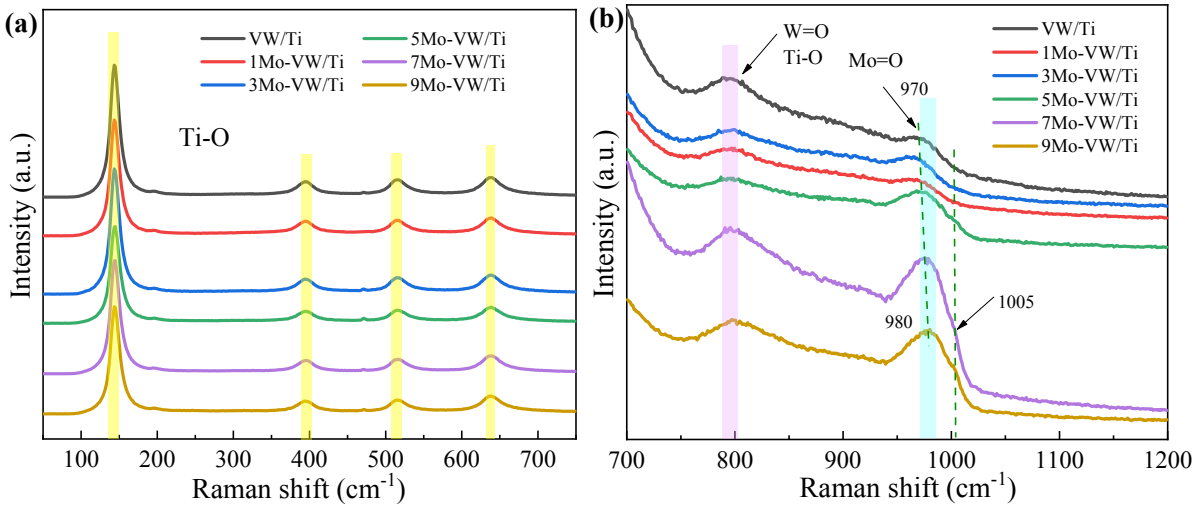

Fig. S3. Raman spectra of the VW/Ti and xMo-VW/Ti (x=1, 3, 5, 7, and 9 wt.%) catalysts at different ranges.

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 occured, indicating more polymeric molybdenum oxide formed.[S1,S10] When the loading amount of MoO_3 exceeded 7 wt.%, a week peak of nearly 1000 cm^{-1} appeared attributed to monomeric surface vanadia or a few crystalline MoO_3 species.[S11]

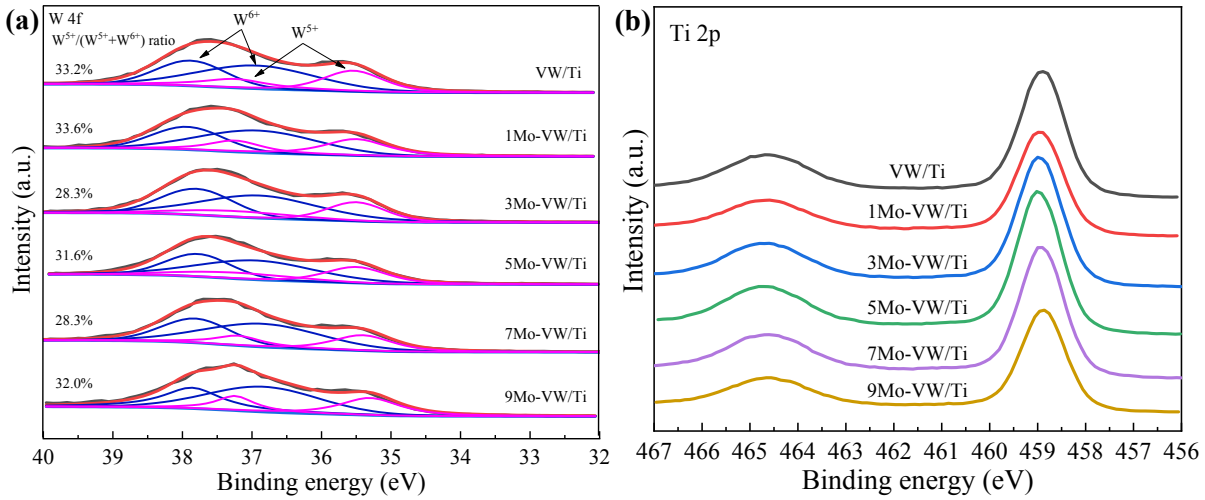

Fig. S4. XPS spectra for (a) W 4f and (b) Ti 2p of the VW/Ti and xMo-VW/Ti (x=1, 3, 5, 7, and 9 wt.%) catalysts.

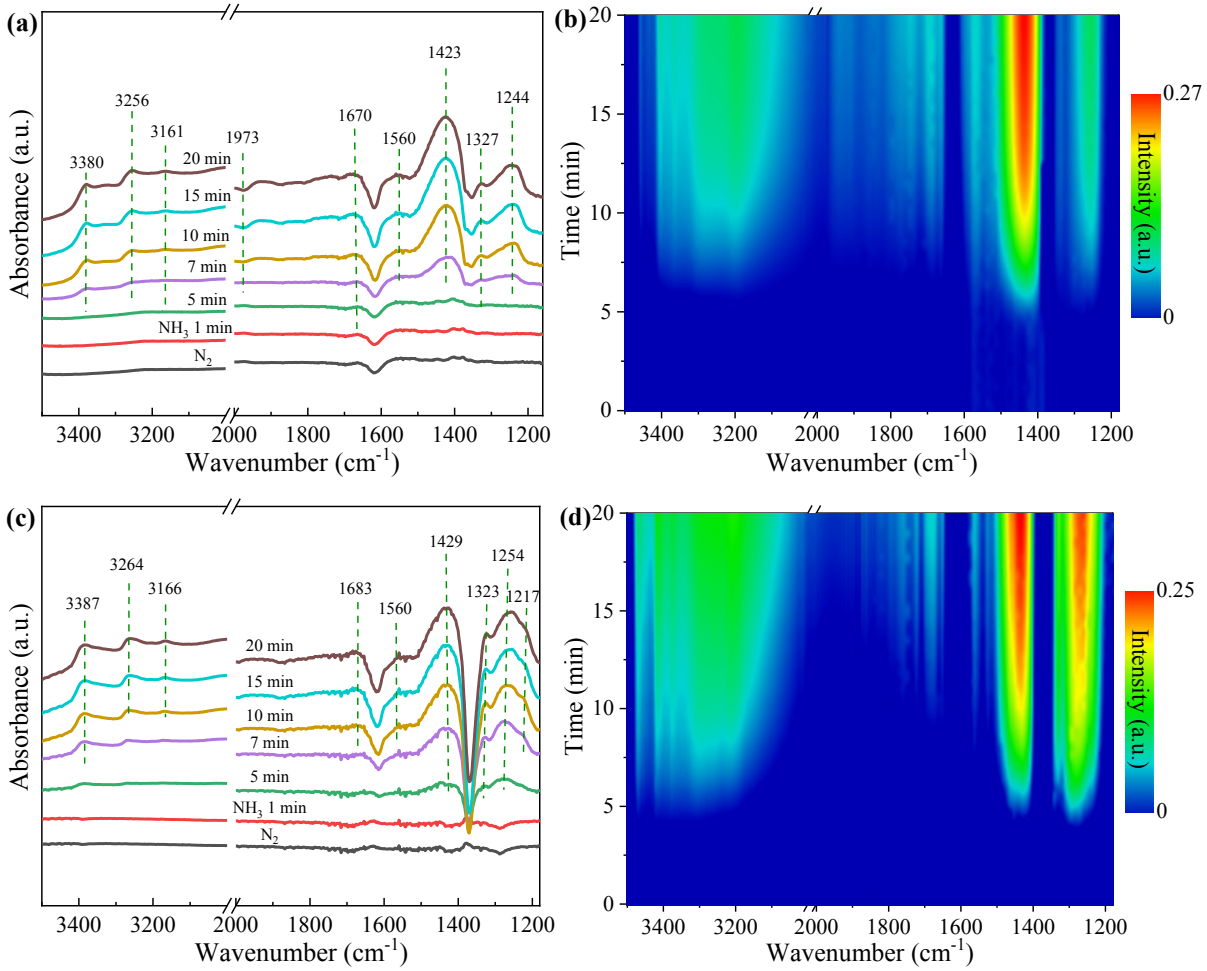

Fig. S5. *In situ* DRIFTs spectra of the (a) 7Mo-VW/Ti and (c) VW/Ti catalysts pretreated by exposure to 600 ppm NO + 6 vol.% O_2 followed by exposure to 600 ppm NH_3 at 250 °C, and the corresponding mapping of the (b) 7Mo-VW/Ti, and (d) VW/Ti catalysts.

Fig. S5 shows the *in situ* DRIFTs spectra of the reaction between pre-adsorbed NO species and gaseous NH_3 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 + O_2 pretreated and N_2 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 NH_4^+(B) (1670 and 1423 cm^{-1}) and NH_3(L) (3380, 3356, 3161, 1244, and 1217 cm^{-1}) species were generated. The weak bands of NH_2 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 NH_3 adsorption, so a negative peak of Mo=O bond (1973 cm^{-1}) was found because of the influence of NH_3 to unsaturated molybdenyl species.

References

[S1] G. Dong, Y. Bai, Y. Zhang and Y. Zhao, *New J. Chem.*, 2015, **39**, 3588-3596.

[S2] Y. Geng, X. Chen, S. Yang, F. Liu and W. Shan, *ACS Appl. Mater. Inter.*, 2017, **9**, 16952-16959.

[S3] W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Appl. Catal. B*, 2012, **115-116**, 100-106.

[S4] C. Wang, S. Yang, H. Chang, Y. Peng and J. Li, *Chem. Eng. J.*, 2013, **225**, 520-527.

[S5] X. Liu, X. Wu, T. Xu, D. Weng, Z. Si and R. Ran, *Chinese J. Catal.*, 2016, **37**, 1340-1346.

[S6] D. W. Kwon, K. H. Park and S. C. Hong, *Chem. Eng. J.*, 2016, **284**, 315-324.

[S7] V. Jadkar, A. Pawbake, R. Waykar, A. Jadhavar, A. Mayabadi, A. Date, D. Late, H. Pathan, S. Gosavi and S. Jadkar, *J. Mater. Sci.: Mater. El.*, 2017, **28**, 15790-15796.

[S8] R. S. Stampel, Y. Chen, J. A. Dumesic, C. Niu and C. G. Hill, *J. Catal.*, 1987, **105**, 445-454.

[S9] Z. Huang, Y. Du, J. Zhang, X. Wu, H. Shen and G. Jing, *Environ. Sci. Technol.*, 2019, **53**, 5309-5318.

[S10] L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giamello, P. Forzatti and F. Bregani, *J. Catal.*, 1999, **187**, 419-435.

[S11] D. W. Kwon, K. H. Park, H. P. Ha and S. C. Hong, *Appl. Surf. Sci.*, 2019, **481**, 1167-1177.