# **Inorganic Chemistry**

# Synthesis of Zeolitic Mo-Doped Vanadotungstates and Their Catalytic Activity for Low-Temperature NH<sub>3</sub>-SCR

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**ABSTRACT:** Mo was successfully introduced into a vanadotungstate (VT-1), which is a crystalline microporous zeolitic transition-metal oxide based on cubane clusters  $[W_4O_{16}]^{8-}$  and  $VO^{2+}$  linkers ( $Mo_xW_{4-x}$ , x: number of Mo in VT-1 unit cell determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES)). It was confirmed that W in the cubane units was substituted by Mo. The resulting materials showed higher microporosity compared with VT-1. The surface area and the micropore volume increased to 296 m<sup>2</sup>·g<sup>-1</sup> and 0.097 cm<sup>3</sup>·g<sup>-1</sup>, respectively, for  $Mo_{0.6}W_{3.4}$  compared with the those values for VT-1 (249 m<sup>2</sup>·g<sup>-1</sup> and 0.078 cm<sup>3</sup>·g<sup>-1</sup>, respectively). The introduction of Mo changed the acid properties including the



SI Supporting Information

acid amount (VT-1: 1.06 mmol  $g^{-1}$ , Mo<sub>0.6</sub>W<sub>3.4</sub>: 2.18 mmol· $g^{-1}$ ) and its strength because of the changes of the chemical bonding in the framework structure. Mo<sub>x</sub>W<sub>4-x</sub> showed substantial catalytic activity for the selective catalytic reduction of NO with NH<sub>3</sub> (NH<sub>3</sub>-selective catalytic reduction (SCR)) at a temperature as low as 150 °C.

## INTRODUCTION

Microporous materials can be exploited for extensive applications because the open space in the micropores provides confined chemical reaction fields with various functions such as molecular sieving, molecular recognition, and shape-selective catalysis. Zeolites are representative microporous materials, which are thermally stable crystalline metal oxides with ordered microporous structures and have high surface areas with solid-acid properties. Zeolites are, therefore, widely used as catalysts in oil-refining and petrochemical industries.<sup>1-3</sup> Although there are many structural variants and elemental diversity in the zeolite family, it is still very hard to introduce redox properties on the basis of transition elements in the zeolitic porous frameworks. If redox properties are intrinsically introduced into the porous framework, the resulting materials can be further utilized in oxidation catalysis, photochemical reactions, and electrochemical reactions. Thus, the discovery and synthesis of ordered porous crystalline transition-metal oxides is an interesting and important topic to create novel functional materials.

Transition-metal elements generally adopt an octahedral coordination state. The use of octahedral building blocks to form porous materials is an interesting approach. However, it is difficult to realize high-dimensional assembling of these polyoctahedra units.<sup>4</sup> Nevertheless, a few microporous transition-metal oxides have been reported. The most well-known materials are microporous manganese oxides, so-called "octahedral molecular sieves" (OMS).<sup>5–7</sup> The OMS constitutes infinite chains of edge-shared MnO<sub>6</sub> octahedra that form a one-dimensional (1D) channel in the crystal. Another typical example is crystalline Mo–V mixed-metal oxides (Mo<sub>3</sub>VO<sub>x</sub>).<sup>8</sup> These materials comprise a structural arrange-

ment based on the pentagonal  $[Mo_6O_{21}]^{6-}$  units and  $MO_6$  (M = Mo, V) octahedra that form a crystalline structure with the micropores of hexagonal and heptagonal channels.

Recently, we reported a new microporous zeolitic transitionm et al oxide based on vanadotungstate,  $(NH_4)_{0.25}K_{1.5}H_{0.25}[W^{VI}_4V^{IV}_3O_{19}]$ .9.5H<sub>2</sub>O (denoted as VT-1), which is composed of  $[W_4O_{16}]^{8-}$  cubane units and VO<sup>2+</sup> linkers.<sup>9</sup> We call this material ZOMO (zeolitic octahedral metal oxide) in short. This material has an open space accessible for small molecules with the molecular size less than 0.43 nm, which results in the considerably high Brunauer–Emmett–Teller (BET) surface area (~300 m<sup>2</sup> g<sup>-1</sup>) despite the use of heavy atoms as constituent elements.

VT-1-based materials exhibit substantial catalytic activity for the selective catalytic reduction of NO with NH<sub>3</sub> (NH<sub>3</sub>-SCR) at low temperatures because of the combination of acidity, redox properties, and high surface area.<sup>9</sup> NH<sub>3</sub>-SCR is a significant reaction because NO is the chief inducer of ozone depletion, acid rain, and global photo-oxidation pollution.<sup>10,11</sup> Vanadium (V) oxide-based catalysts (V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ TiO<sub>2</sub>) have been widely used in industries because of the high N<sub>2</sub> selectivity and good thermal stability.<sup>12</sup> However, such catalysts require a working temperature as high as 300 °C. Therefore, the SCR system has to be placed just after the boiler followed by the electric precipitator and the deSO<sub>x</sub> system.

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The catalyst is directly exposed to SO<sub>x</sub> and ash, and it is easily deactivated by the sulfates and ash.<sup>13</sup> This problem can be solved if a catalyst is effective at a temperature lower than 150 °C. Up to now, various catalysts have been prepared and applied in low-temperature-selective catalytic reduction (LT-SCR) such as transition-metal oxides (Fe, V, Cr, Cu, Co, and Mn)<sup>14–17</sup> and Cu/Fe ion-exchanged zeolite (Cu-ZSM-5 and Fe-ZSM-5).<sup>18,19</sup> Particularly, manganese-containing catalysts have attracted much attention because of their variable valence states and excellent redox ability.<sup>20,21</sup> However, these catalysts exhibit lower N<sub>2</sub> selectivity, and they usually produce N<sub>2</sub>O as a byproduct.<sup>22</sup> Hence, the development of catalysts that show both good low-temperature activity and high N<sub>2</sub> selectivity is of great importance for the NH<sub>3</sub>-SCR reaction. VT-1 is exactly one of the excellent candidates that show high efficiency for NH<sub>3</sub>-SCR at low temperatures with 100% N<sub>2</sub> selectivity.

It is known that the properties of transition-metal oxides, such as redox property, acidity, and magnetic properties are tunable by combining component elements.<sup>23,24</sup> We attempted to expand the elemental diversity of VT-1 to realize multifunctionality. In the present study, we report a series of Mo-doped vanadotungstates  $[Mo_{x}^{VI}W^{I}_{4-x}V^{IV}_{3}O_{19}]^{2-}$  $(Mo_{x}W_{4-x}$ . x means the substitution amount of W by Mo determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES)) (Figure 1). The redox property,



**Figure 1.** Structural models of VT-1 and Mo-substituted VT-1. Blue: W; gray: V; pink: a mixture of Mo and W; red: O; purple: K.

porosity, and acidity of VT-1 were enhanced by the introduction of Mo, and the Mo-substituted VT-1 materials exhibited higher efficiency for NH<sub>3</sub>-SCR at low temperatures.

# **EXPERIMENTAL SECTION**

Synthesis of  $[W_4V_3O_{19}]^{2-}$  (VT-1). Ammonium paratungstate hydrate (abbreviated as APT, 2.5533 g, 10 mmol of W) was dissolved in 15 mL of KOH (2.1784 g, 33 mmol) aqueous solution. After acidification with 6 mL of  $H_2SO_4$  (2 M), 10 mL of VOSO\_4 (2.0571 g, 8 mmol) aqueous solution was added. After adjusting the pH of the solution to 4.0 by adding NH<sub>4</sub>OH (28%), the mixed solution was subjected to the hydrothermal synthesis at 175 °C for 24 h. The crude solid formed in the hydrothermal reaction was separated by centrifugation (5000 rpm, 4 min), dispersed in 20 mL of deionized water, and centrifuged (2000 rpm, 2 min) several times to remove undesired solids. Green solids were obtained from the upper turbid liquid by high-speed centrifugation (8000 rpm, 15 min) and dried at 80 °C overnight. The yield of VT-1 was 86.5% based on W. The yields of these materials were calculated on the basis as the ratio of the solid weights after centrifugation and the theoretical value based on the amount of W used.

Synthesis of  $[Mo_xW_{4-x}V_3O_{19}]^{2-}$   $(Mo_xW_{4-x})$ . The  $Mo_xW_{4-x}$  materials were prepared using the same method as that for preparing VT-1, with different ratios of APT to ammonium heptamolybdate hydrate (abbreviated as AHM). The W/Mo mole ratios and the corresponding yields are as follows: APT (9.5 mmol of W) to AHM (0.5 mmol of Mo) for  $Mo_{0.2}W_{3.8}$  with a yield of 82.5%, APT (9.0 mmol of W) to AHM (1.0 mmol of Mo) for  $Mo_{0.4}W_{3.6}$  with a yield of 74.3%, APT (8.0 mmol of W) to AHM (2.0 mmol of Mo) for

 $Mo_{0.6}W_{3.4}$  with a yield of 62.2%, APT (7.5 mmol of W) to AHM (2.5 mmol of Mo) for  $Mo_{0.7}W_{3.3}$  with a yield of 53.4%, APT (7.0 mmol of W) to AHM (3.0 mmol of Mo) for  $Mo_{0.8}W_{3.2}$  with a yield of 45.1%, and APT (6.0 mmol of W) to AHM (4.0 mmol of Mo) for  $Mo_{1.0}W_{3.0}$  with a yield of 29.3%. The atomic ratios obtained by ICP and energy-dispersive X-ray (EDX) analyses are presented in Table S1. It was assumed that the occupation of W in the cubane unit is four in VT-1. The total amount of W + Mo should be four. Hereafter, the data were calculated based on this rule.

Characterization. X-ray diffraction (XRD) measurements were carried out with an Ultima III X-ray diffractometer (Rigaku, Japan) with Cu-K $\alpha$  radiation (tube voltage: 40 kV, tube current: 40 mA). Fourier-transform infrared (FT-IR) spectra were obtained on a JASCO-FT/IR-4100 instrument (JASCO. Japan). Diffuse reflectanceultraviolet-visible (DR-UV-vis) spectra were recorded using a JASCO V-550 UV-vis spectrophotometer equipped with an ISN-470 reflectance spectroscopy accessory (JASCO, Japan), and using BaSO<sub>4</sub> as a diluter. X-ray photoelectron spectroscopy (XPS) was performed on a JPS-9010MC (JEOL) instrument after Au coating (SC-701 MkII, Sanyu Electron) the specimen. The spectrometer energies were calibrated using the Au 4f 7/2 peak at 84.0 eV. Raman spectra (inVia Reflex Raman spectrometer, JASCO) were obtained in air using a static sample, with an Ar laser (532 nm). The peak position was calibrated relative to the Si peak at 520 cm<sup>-1</sup>. The elemental composition of the bulk sample was measured by ICP-AES (ICPE-9820, Shimadzu). Temperature-programmed desorption (TPD) measurements were carried out using a TPD apparatus (BEL Japan, Inc., Japan) equipped with a quadrupole mass spectrometer. Samples (50 mg) were placed between two layers of quartz wool. The TPD of  $NH_3$  (m/z = 16) and  $H_2O$  (m/z = 18) was measured by increasing the temperature from 40 to 500 °C at a heating rate of 10 °C minunder He flow (flow rate: 50 mL min<sup>-1</sup>). Thermal gravimetrydifferential thermal analysis (TG-DTA) was carried out from room temperature to 500 °C at a heating rate of 10 °C min<sup>-1</sup> under nitrogen flow (flow rate: 50 mL min<sup>-1</sup>) on a Thermo Plus EVO2 TG-DTA8122 (Rigaku, Japan) instrument. Gas adsorption experiments were carried out on a BELsorp Max system (BEL, Japan). Before the adsorption experiments, the materials were heat-treated at 175 °C for 2.5 h under vacuum. N2 adsorption measurements were conducted at the liquid N<sub>2</sub> temperature  $(-196 \, ^{\circ}C)$ . The surface area and pore volume were estimated using the Brunauer-Emmett-Teller (BET) method and t-plot method, respectively. The structures of Mo<sub>x</sub>W<sub>4-x</sub> were refined by powder XRD Rietveld refinement using Materials Studio 7.1 (Accelrys Software Inc.).

NH<sub>3</sub>-SCR. NH<sub>3</sub>-SCR was conducted over Mo<sub>x</sub>W<sub>4-x</sub> catalysts using a fixed-bed reactor at atmospheric pressure. Before the reactions, the Mo<sub>x</sub>W<sub>4-x</sub> catalysts were treated at 220 °C under a 250 mL min<sup>-1</sup> flow of Ar for 1 h. After the system cooled to a set temperature, the reaction gas was introduced at a flow rate of 250 mL min<sup>-1</sup>. The gas comprised NO (250 ppm), NH<sub>3</sub> (250 ppm), and O<sub>2</sub> (4 vol %), with Ar as a diluter. The catalytic reaction was carried out at set temperatures of 120 °C. The reactants and products were analyzed with an FT-IR instrument (FT/IR-4700ST, JASCO) equipped with a gas cell (LPC-12 M-S, light path length 12 m, JASCO). The standard NH<sub>3</sub>-SCR reaction is represented by eq 1. No byproducts such as NO and N<sub>2</sub>O were observed during the NH<sub>3</sub>-SCR, and the selectivity for N<sub>2</sub> was 100%. The respective catalytic parameters were calculated as follows:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + H_2O$$
 (1)

NO conversion [%] = 
$$(NO_{in} - NO_{out})/NO_{in} \times 100$$
 (2)

$$NH_3 \text{ conversion } [\%] = (NH_{3in} - NH_{3out})/NH_{3in} \times 100$$
(3)

$$N_{2} \text{ selectivity } [\%] = 2 \times N_{2\text{out}} / [(\text{NO}_{\text{in}} + \text{NH}_{3\text{in}}) - (\text{NO}_{\text{out}} + \text{NH}_{3\text{out}})] \times 100$$
(4)

## RESULTS AND DISCUSSION

Synthesis and Characterization of  $Mo_xW_{4-x}$ . A series of  $Mo_xW_{4-x}$  catalysts with varying x were synthesized. Figure 2



Figure 2. Changes in the amount of W and V as a function of the amount of Mo in the  $Mo_xW_{4-x}$  unit.

shows the changes in the amount of W and V as a function of x. The W/V ratio of pristine VT-1 was 4.0/3.0, which matches well with the reported value.<sup>9</sup> The introduction of Mo was accompanied by a continuous decrease in the amount of W. However, the amount of V in the bulk was constant despite the increase in x, up to x = 1.0, and the (Mo + W)/V ratio of Mo<sub>x</sub>W<sub>4-x</sub> remained consistent at 4.0/3.0. When the preparative composition of Mo to W was increased to 2.0/2.0 (x = 2.0), the elemental composition changed drastically. The elemental composition became Mo/W/V = 2.0/2.0/2.0, implying that the obtained material has no longer the VT-1 structure.

The color of  $Mo_xW_{4-x}$  changed by changing the amount of Mo in solids (Figure S1). VT-1 was green,  $Mo_xW_{4-x}$  (x = 0.6-0.8) was light brown,  $Mo_{1.0}W_{3.0}$  was dark brown, and the color of  $Mo_{0.2}W_{3.8}$  and  $Mo_{0.4}W_{3.6}$  was yellow-green, which was the transition color between VT-1 and  $Mo_{0.6}W_{3.4}$ . The morphology and size of VT-1 and  $Mo_xW_{4-x}$  were studied by scanning electron microscopy (SEM) (Figure S2). It showed that they were cube-shaped materials with the diameter of ca. 50 nm. It showed that the morphology of the materials did not significantly change after Mo was introduced.

XRD measurements were carried out for  $Mo_xW_{4-x}$ . The XRD peaks at  $2\theta = 10.3$ , 14.6, and 17.1° and  $2\theta = 21.0-36.0°$  were attributable to the VT-1 structure,<sup>9</sup> and the patterns of  $Mo_xW_{4-x}$  ( $x \le 1.0$ ) were almost the same as that of pristine VT-1, except for the small peak shifts and peak broadening, particularly at x = 1.0 (Figure S3). No XRD peaks attributable to the VT-1 structure were observed when the elemental composition of Mo was higher than 1.0, and new XRD peaks that are not identified appeared (Figure 3a). On the basis of the ICP and XRD results, we concluded that less than one W among four W in the cubane unit could be replaced by Mo,



**Figure 3.** XRD patterns of  $Mo_xW_{4-x}$  (a) and lattice parameters after Rietveld refinement (b).

and further addition of Mo resulted in the formation of unidentified materials.

The lattice parameters of  $Mo_xW_{4-x}$  calculated by the Reitveld refinement (Figure S4) are shown in Figure 3b. The lattice parameters decreased continuously with increasing *x*, suggesting the introduction of Mo into the VT-1 structure. In fact, the ionic radius of  $Mo^{6+}$  (0.59 Å) is smaller than that of  $W^{6+}$  (0.60 Å) in octahedral coordination; thus, the decrease in the lattice parameters with the introduction of Mo is reasonable. This result, as well as the results of elemental analysis, clearly reveal that W in the cubane units is partially replaced by Mo.

FT-IR, Raman, and DR UV-vis analyses were carried out to investigate the state of the chemical bonds in the VT-1 structure. The IR band at 975 cm<sup>-1</sup> is attributable to the weakly bound V=O in square pyramidal coordination in the linker, and the band at 900 cm<sup>-1</sup> is assigned to the  $V-O_{\rm b}-$ W(Mo)of bridging oxygen between the cubane and the linker; the signals at 810 and 590 cm<sup>-1</sup> were assigned to cornersharing W(Mo) $-O_c-W$  in the cubane (Figure S5a).<sup>25–27</sup> The IR bands at 810 and 590 cm<sup>-1</sup> were continuously red-shifted with x (Figure S5b), clearly supporting the replacement of W with Mo in the cubane unit. Figure S6a shows the Raman spectra of  $Mo_xW_{4-x}$ . The peaks at 960 and 910 cm<sup>-1</sup> are assigned to the symmetrical stretching vibration and asymmetric stretching vibration of the W-O<sub>c</sub>-W bond, respectively.<sup>28</sup> The peak at 1005 cm<sup>-1</sup> is attributed to V=  $\rm O.^{29}$  A shoulder peak of the Mo–O–W band at 880  $\rm cm^{-1}$  was observed in the Raman spectra of Mo<sub>x</sub>W<sub>4-x</sub>, suggesting the incorporation of Mo into the VT-1 structure.<sup>30-32</sup> The intensity of the peak attributed to W-Oc-W decreased as the amount of the Mo dopant increased, particularly when x exceeded 0.6. Simultaneously, the intensity of the Mo-O-W band increased with x (Figure S6b).

In the case of the DR UV–vis analyses (Figure 4a), the absorption bands at 390 nm are attributable to the intervalence



Figure 4. UV–vis spectra of  $Mo_xW_{4-x}$  (a) and absorbance at 390 and 530 nm (b): black: VT-1, red:  $Mo_{0.2}W_{3.8}$ , blue:  $Mo_{0.4}W_{3.6}$ , green:  $Mo_{0.6}W_{3.4}$ , pink:  $Mo_{0.7}W_{3.3}$ , brown:  $Mo_{0.8}W_{3.2}$ , and dark-blue:  $Mo_{1.0}W_{3.0}$ .

charge transfer (IVCT) in V<sup>4+</sup>–O–W<sup>6+</sup>. After the introduction of Mo, the adsorption of V<sup>4+</sup> at 660 and 860 nm was constant.<sup>9,33</sup> The absorption of the IVCT of the V<sup>4+</sup>–O–Mo<sup>6+</sup> unit clearly increased with x, accompanied by a decrease in the IVCT derived from V<sup>4+</sup>–O–W<sup>6+</sup> (Figure 4b). This observation is consistent with the FT-IR data, which further confirmed that Mo was indeed introduced into the VT-1 structure by replacing W in the cubane unit.

It was confirmed that the amount of W in VT-1 decreased, while the amount of Mo increased. There are two possibilities of the Mo position: (1) W in the cubane units is randomly replaced by Mo and (2) Mo atoms exist in one cubane unit, while they do not exist in another cubane unit. In order to figure out the location site of Mo in the VT-1 structure, we have built two structure models and carried out XRD simulation experiments (Figure S7). The XRD patterns simulated from the structural model (1) were almost the same with the experimentally obtained XRD patterns. However, a new peak at 7.3° appeared in the XRD patterns simulated from the structural model (2), which was not observed in the experimental samples. The simulated XRD patterns strongly suggested that Mo atoms just statistically locate throughout the cubane unit. The redshift observed using FT-IR, Raman, and UV-vis spectroscopy techniques further implied that the Mo atoms were statistically introduced in the W cubane unit, and W-O-V or W-O-W bonds were affected by Mo. While if Mo was located independently as cubane, the chemical bonds of W-O-W are considered to be changed significantly.

 $Mo_xW_{4-x}$  was subjected to XPS in order to investigate the oxidation states of the constituent elements (Figures S8–10). The Mo XPS profile showed two peaks at 235.6 and 232.3 eV assignable to the  $3d_{3/2}$  and  $3d_{5/2}$  states of  $Mo^{VI}$ , respectively.<sup>34</sup> The two peaks at 37.8 and 35.8 eV are attributed to the  $4f_{5/2}$  and  $4f_{7/2}$  states of  $W^{VI}$ , respectively.<sup>35</sup> The peak at 517.0 is derived from  $V^{IV}$  ( $2p_{3/2}$ ).<sup>36</sup> The oxidation states of Mo, W, and V in the cubane unit were constant regardless of the increase in x, which indicated that the introduction of Mo did not change the oxidation states of the other constituent elements of VT-1. The composition of each element calculated from the XPS data is presented in Table S1. The Mo and W compositions were consistent with the results of ICP and EDX, which suggests that the elemental composition of Mo and W in the bulk and on the surface of the materials is the same. The amount of V determined by XPS was less, possibly due to the fact that V did not occupy all the linker on the surface.

Thermal Stability. The TPD analysis of the materials demonstrated that the removal of  $H_2O$  occurred at ~100 °C. Two peaks corresponding to NH<sub>3</sub> desorption were observed at 100 and 300 °C (Figure S11). The TG-DTA indicated about 10% weight loss around 100-200 °C (Figure S12), which is attributed to the removal of water molecules and NH<sub>3</sub> from  $Mo_rW_{4-r}$ . According to the fact that the weight loss around 100-200 °C can be almost attributable to the desorption of water (Figure S11), we calculated the chemical formulas of  $Mo_xW_{4-x}$  based on the results of ICP, TPD, and TG as follows:  $Mo_{0.2}W_{3.8}$ :  $(NH_4)_{0.25}K_{1.5}H_{0.25}[Mo_{0.2}W_{3.8}V_3O_{19}]$ . 6.8 $H_2O$ ;  $Mo_{0.4}W_{3.6}$ :  $(NH_4)_{0.25}K_{1.5}H_{0.25}[Mo_{0.4}W_{3.6}V_3O_{19}]$ . 6.1H<sub>2</sub>O;  $Mo_{0.6}W_{3.4}$ :  $(NH_4)_{0.25}K_{1.5}H_{0.25}[Mo_{0.6}W_{3.4}V_3O_{19}]$ . 6.5H<sub>2</sub>O;  $Mo_{0.7}W_{3.3}$ :  $(NH_4)_{0.25}K_{1.5}H_{0.25}[Mo_{0.7}W_{3.3}V_3O_{19}]$ . 5.9 $H_2O$ ;  $Mo_{0.8}W_{3.2}$ :  $(NH_4)_{0.25}K_{1.5}H_{0.25}[Mo_{0.8}W_{3.2}V_3O_{19}]$ . 6.2H<sub>2</sub>O;  $Mo_{1.0}W_{3.0}$ :  $(NH_4)_{0.25}K_{1.5}H_{0.25}[Mo_{1.0}W_{3.0}V_3O_{19}]$ . 6.4H<sub>2</sub>O. The exothermic peak around 300 °C was assigned to the desorption of NH<sub>3</sub>, because the  $Mo_xW_{4-x}$  materials began to collapse above 300 °C. The endothermic peak around 400–450 °C corresponds to the phase transformation between the two unknown phases. The materials were stable up to 250 °C in N<sub>2</sub> without changes in the XRD and FTIR spectra (Figure S13). Therefore, water can be removed by calcination without decomposing the material structure at this temperature.

The stability of the  $Mo_xW_{4-x}$  materials can also be calculated theoretically by applying density functional theory (DFT). The structures of  $Mo_xW_{4-x}$  were optimized by DFT, and the formation energies of  $Mo_x W_{4-x}$  were obtained and plotted, as shown in Figure S14. The lowest formation energy of -711.36kJ·mol·atom was observed for VT-1. The formation energy increased gradually as the amount of Mo increased, indicating that the stability of  $Mo_x W_{4-x}$  decreased continuously with increasing *x*. This observation may account for why the substitution limit is one in four W in the cubane.

 $N_2$  Adsorption Properties. The microporosity of  $Mo_xW_{4-x}$  was investigated by  $N_2$  adsorption-desorption measurements at liquid  $N_2$  temperature (Figure 5). All the



**Figure 5.** N<sub>2</sub> adsorption isotherm of  $Mo_x W_{4-xi}$  blank: VT-1, red:  $Mo_{0.2}W_{3.8'}$  blue:  $Mo_{0.4}W_{3.6'}$  dark cyan:  $Mo_{0.6}W_{3.4'}$  pink:  $Mo_{0.7}W_{3.3'}$  dark yellow:  $Mo_{0.8}W_{3.2'}$  and navy:  $Mo_{1.0}W_{3.0}$ .

materials showed N<sub>2</sub> uptake in the quite low-pressure range  $(P/P_0 < 10^{-5})$ , indicating the microporosity of these materials. The external surface area and the micropore volume of the materials estimated from the t-plot are shown in Table 1. The

Table 1. External Surface Area and Micropore Volume of  $Mo_xW_{4-x}$  Based on  $N_2$  Adsorption Isotherms and Acid Site Distribution Based on  $NH_3$ -TPD

samples	external surface area $(m^2 g^{-1})$	micropore volume (cm <sup>3</sup> g <sup>-1</sup> )	total acidity (mmol/g)	peak area ratio 250 °C/180 °C
VT-1	49	0.078	1.06	0.51
$Mo_{0.2}W_{3.8}$	52	0.082	1.24	0.53
$Mo_{0.4}W_{3.6}$	57	0.084	1.69	0.64
$Mo_{0.6}W_{3.4}$	60	0.097	2.18	0.82
Mo <sub>0.7</sub> W <sub>3.3</sub>	61	0.083	2.02	0.90
$Mo_{0.8}W_{3.2}$	62	0.072	0.95	1.07
$Mo_{1.0}W_{3.0}$	64	0.061	0.84	1.23

micropore volume of  $Mo_x W_{4-x}$  increased as x increased up to 0.7. The increase in the micropore volume cannot be explained by the change in the amount of K<sup>+</sup> in the micropores because the amount of  $K^{\scriptscriptstyle +}$  in the structure was almost the same regardless of x. It is proposed that the slight change in the location site of K<sup>+</sup> in the pore may account for the observed increase in the microporosity. As implied by geometry optimization calculations (Figure S15), the distance between K<sup>+</sup> and W, V atoms was 3.614 and 3.514 Å for x = 0.6, which is smaller than those in VT-1 (3.717 and 3.538 Å). The position of K<sup>+</sup> in Mo<sub>0.6</sub>W<sub>3.4</sub> was closer to that in the cubane unit and that in VT-1, which left more space in the micropore of  $Mo_{0.6}W_{3.4}$  to absorb more N<sub>2</sub> molecules. Undoubtedly, further analyses are necessary to clearly understand this improvement. Further increasing the amount of Mo resulted in a decrease in the micropore volume. When x exceeded 0.8, the crystallinity decreased, as indicated by the XRD measurements. This observation suggests poor micropore texture when x exceeds 0.8, which may be the reason for the decreased microporosity (Table 1).

Acidity Characterization. The temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) is one of the most conventional methods for characterizing acidity in porous materials because the small size of ammonia allows the quantitative analysis of almost all the acid sites in micro-, meso-, and macroporous oxides.<sup>37</sup> The NH<sub>3</sub>-TPD data for VT-1 and  $Mo_x W_{4-x}$  are presented in Figures S16-17. The materials showed two NH<sub>3</sub> desorption peaks at 180 and 250 °C after the adsorption of NH<sub>3</sub> at 100 °C; the area ratios of the two peaks are summarized in Table 1. Compared with the conventional VT-1, the introduction of Mo increased the peak area for NH<sub>3</sub> desorption at 250 °C, which indicates that the amount of stronger acid sites increased with the incorporation of Mo. Some chemical bonds in Mo<sub>x</sub>W<sub>4-x</sub> changed from W-O-V to Mo-O-V, which may lead to variations in the electron density of the Mo, W, and V atoms; thus, the total acidity and acid strength also changed. In addition, the microporosity of the materials was adjusted by the introduction of Mo, which exhibited the same trend with the total acidity. Therefore, the microporosity also made contributions to the adsorption of NH<sub>3</sub>.

**Catalytic Activity.** NO conversion in the NH<sub>3</sub>-SCR over the VT-1 and Mo<sub>x</sub>W<sub>4-x</sub> (x = 0.4, 0.6) catalysts was measured at the reaction temperature of 150 °C (Figure 6). The catalytic



**Figure 6.** Catalytic activity of VT-1 and  $Mo_xW_{4-x}$  (x = 0.4, 0.6) for NH<sub>3</sub>-SCR at 150 °C. Reaction conditions: NO: 250 ppm, NH<sub>3</sub>: 250 ppm, 4 vol % of O<sub>2</sub> in Ar, flow rate: 250 mL/min, catalysts: 375 mg.

activity of the materials was constant over the entire reaction time studied, and the XRD patterns did not change significantly after the reactions (Figure S18). No formation of byproducts such as NO and N<sub>2</sub>O during the NH<sub>3</sub>-SCR was observed; thus, the selectivity for N<sub>2</sub> was 100%. The NO conversion over VT-1 was around 50%.  $Mo_xW_{4-x}$  (x = 0.4, 0.6) also promoted NO conversion at 150 °C, and the activity was slightly higher than that of VT-1 (NO conversion = ca. 60%). There are many considerable reasons about the improvement of the catalytic activity, including the change of the acid properties, microporosity as catalysis field, oxidation state during the reaction, and so forth. The critical factors for the improvement of the catalytic activity are currently under investigation based on the study of the reaction mechanism.

## CONCLUSIONS

A series of Mo-doped vanadotungstate materials  $Mo_xW_{4-x}$  (x = 0.2-1.0) were successfully synthesized, and W was substituted by Mo in the cubane units. The maximum amount of Mo introduced into the system was 1.0. The introduction of Mo increased the porosity (micropore volume increased from 0.078 cm<sup>3</sup>/g of VT-1 to 0.097 cm<sup>3</sup>/g of Mo<sub>0.6</sub>W<sub>3.4</sub>), and the

acidity increased from 1.06 mmol/g for VT-1 to 2.18 mmol/g for  $Mo_{0.6}W_{3.4}$ . The introduced Mo also showed catalytic activity for the NH<sub>3</sub>-SCR at a temperature as low as 150 °C, with 60% NO conversion and 100% N<sub>2</sub> selectivity.

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00107.

Color of solids, crystal morphology, XRD patterns, results of the Rietveld refinement, FT-IR, Raman, XPS, TPD-MS, TG-DTA, and the elemental analysis of  $Mo_xW_{4-x}$  (PDF)

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#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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