

Supporting Information for “Efficient One-step Oxidation of Isobutylene to Methacrylic Acid over Mo-V-Te-Cs by Integrating Active Lattice Oxygen and Suitable Medium Acidity”

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1 Experimental

1.1 Materials

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, H_6TeO_6 , and $\text{C}_2\text{H}_5\text{OH}$ were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Company Limited). NH_4VO_3 , $\text{Ce}(\text{NO}_3)_4$, $\text{Ti}(\text{SO}_4)_2$, $\text{Ga}(\text{NO}_3)_3$, $\text{In}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2$ were of analytical grade and purchased from Aladdin Biochemical Technology Co., Ltd. $\text{C}_4\text{H}_6\text{O}$ (95%) and $\text{C}_4\text{H}_6\text{O}_2$ (98%) were purchased from Aladdin Biochemical Technology Co., Ltd. CsNO_3 , $\text{H}_{28}\text{N}_6\text{O}_{41}\text{W}_{12}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, AgNO_3 , and $\text{La}(\text{NO}_3)_3$ were of analytical grade and purchased from Macklin Biochemical Co., Ltd. O_2 (20%)/ N_2 (80%), and *i*- C_4H_8 (99.9%) were purchased from Panjin Tongyu Gas Co., Ltd. Deionized water was used for all experiments.

1.2 Catalyst preparation

4.9 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and 1.4 g NH_4VO_3 were weighed and transferred to a 100 mL three-necked flask and 30 mL of deionized water was added. The three-necked flask was placed in a magnetic stirrer and stirred at 80°C and 500 rpm for about 30 min, when the solids were completely dissolved and the system turned into a light yellow solution. Subsequently, 0.3 g telluric acid was added to the above solution, which turned dark yellow, and 0.8 mmol of salt of the doped element was weighed and dissolved in 5 mL of deionized water in an ultrasonic wave. The salt solution was added to the above solution and stirred at 80°C and 500 rpm for 2 h. Afterwards, the temperature was raised to 110°C, keep at 500 rpm and stirred for about 6 h until only solid material remained in the three-necked flask.

The solids were dried in a drying oven at 110°C for 12 h. The dried solids were then ground in an agate mortar and finally calcined in a tube furnace in a ceramic crucible at 600°C for 4 h at a heating rate of 2°C/min. The calcined solid powder was the Mo-V-Te-Ce catalyst.

1.3 Characterization

Scanning electron microscopy (SEM) using Nova Nano SEM 450, which was produced by FEI Company in USA. Transmission electron microscope (TEM) using Tecnai G2 F30, which was produced by FEI Company in USA. X-ray diffraction (XRD-7000S, Shimadzu, Japan) was identified with a Cu $K\alpha$ radiation in the range of 20-80° (2 θ), 2°/min. Fourier Transform infrared spectroscopy (FTIR) using Nicolet is50, which was produced by Thermo Fisher in USA. Raman spectra using inVia, which was produced by Renishaw in UK. X-ray photoelectron spectroscopy (XPS) data were collected by an ESCALAB™ 250Xi (Thermo Fisher, USA) electron spectrometer using Al- $K\alpha$ radiations. NH_3 temperature-programmed desorption (NH_3 -TPD) were performed by Chemstar TPx, which was produced by Quantachrome in USA.

1.4 Isobutylene oxidation experiments

The device used in the isobutylene oxidation experiment is a fixed-bed reactor built by the laboratory, and the specific flow is shown in Figure S1. Isobutylene gas and air flow from the gas cylinder, the two gases flow through their respective mass flow meters, and the gas flow is controlled by adjusting the flow meters through the controller so that $V_{\text{Air}}:V_{i\text{-C}_4\text{H}_8} = 20:2$, and then the gas passes through the preheater at 200°C for preheating and mixing to obtain the reaction gas. The reaction gas flows into the reaction tube in the fixed bed reactor at 450°C for catalytic oxidation reaction. After the gas passes through the reaction tube, the product is condensed and enters the trap bottle with ethanol for collection, while the gas sampling bag is used to collect the gas components, and the tail gas is exhausted through the pipeline.

The experimental procedure of the isobutylene oxidation reaction was as follows: first, quartz wool was loaded into the corresponding position of the reaction tube for fixation, and an appropriate amount of 40~80 mesh quartz sand was weighed and filled. After that, 1.0 g of catalyst was weighed and filled into the fixed-bed reaction tube and shaken for uniform distribution. Finally, the same amount of quartz sand and quartz wool were filled in turn for fixing.

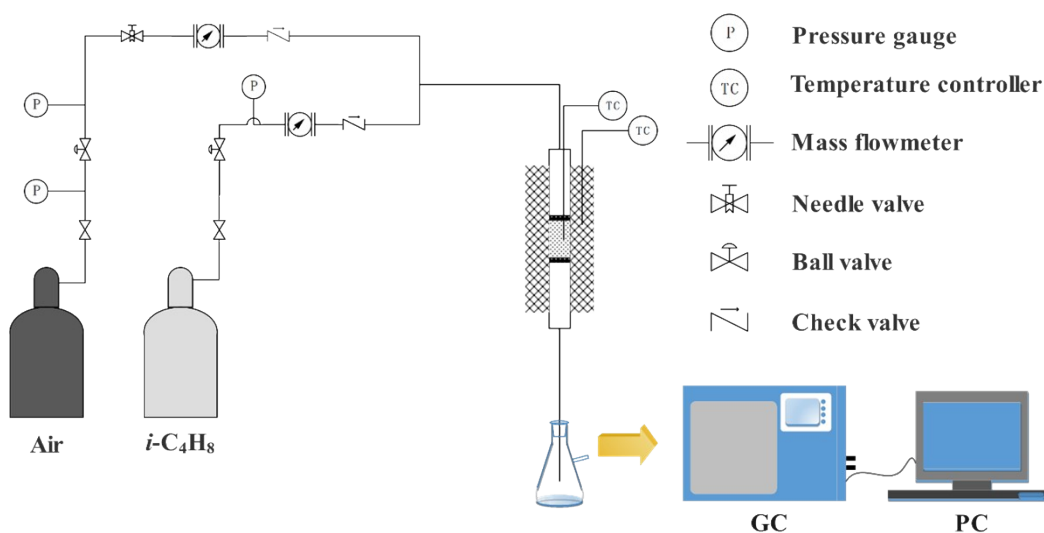


Fig. S1 Schematic of isobutene oxidation reaction equipment

After the reaction finished, the liquid in the trap bottle was acquired and volume with ethanol. Subsequently, the filtrate was filtered using an organic filter membrane, and the content of the product was detected by GC-FID. The column was a capillary column with a length of 30 m, an inner diameter of 320 μm and a film thickness of 0.25 μm . The GC detection conditions were as follows: a FID hydrogen flame ion detector was used, and the column was set up with an initial column temperature of 50°C, maintained for 0.5 min, then ramped up to 70°C at 10°C/min, and then ramped up to 150°C at 20°C/min. Both the inlet and post-detector temperatures were set to 250°C. The column was then ramped up to 70°C at 10°C/min and then to 150°C at 20°C/min.

Product post-processing method: Firstly, ethanol solutions of different concentration gradients of MAL and MAA were configured and their corresponding peak areas were detected using GC, with the horizontal coordinate as the concentration and the vertical coordinate as the peak area for graphing, and the standard curves of MAL and MAA with good correlation could be obtained.

The standard curve of gas isobutene is plotted in the same way, using gas sampling bags to collect different concentrations of $i\text{-C}_4\text{H}_8/\text{Air}$, and using GC to detect the peak areas of different concentrations of gas, with the horizontal coordinate as the concentration of the gas and the vertical coordinate as the peak area for plotting, we can get the standard curve of isobutene with good correlation.

$$\text{Conversion of isobutene} = (\text{moles of reacted } i\text{-C}_4\text{H}_8 / \text{moles of raw material supplied } i\text{-C}_4\text{H}_8) \times 100\%$$

$$\text{Selectivity of MAL, MAA} = (\text{moles of MAL or MAA produced} / \text{moles of } i\text{-C}_4\text{H}_8 \text{ reacted}) \times 100\%$$

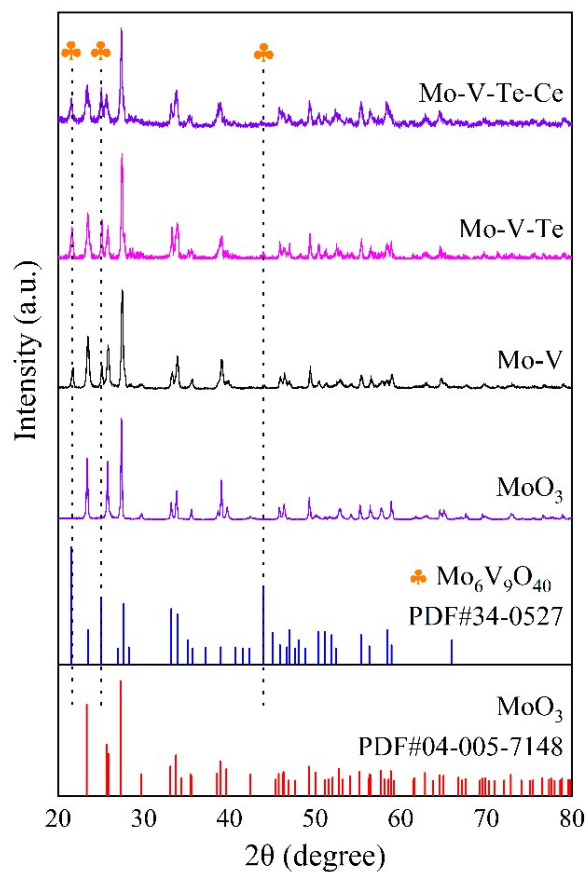


Fig. S2 X-ray diffraction pattern of the samples.

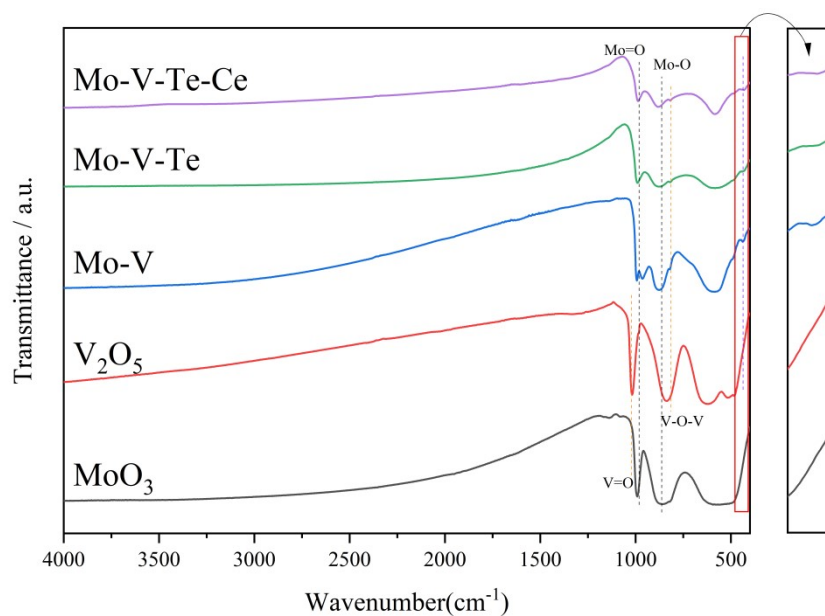


Fig. S3 FT-IR of the samples (a) MoO₃ (b) V₂O₅ (c) Mo-V (d) Mo-V-Te (e) Mo-V-Te-Cs (f) Mo-V-Te-Ti

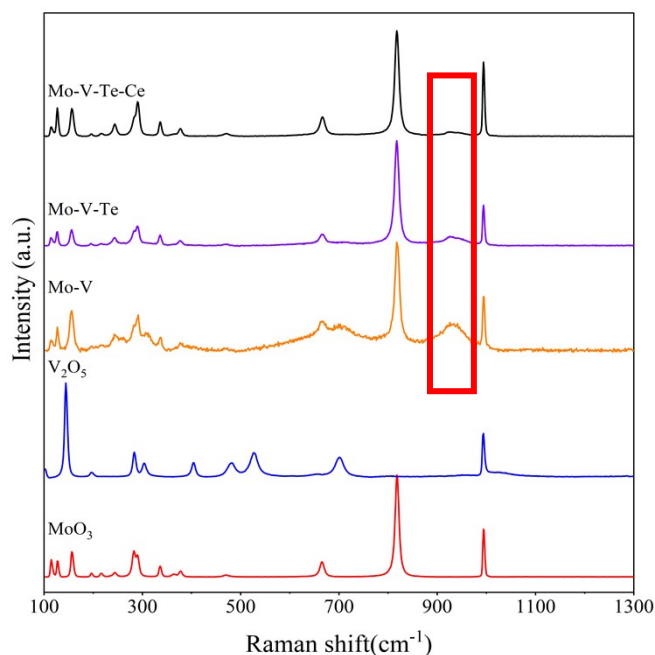


Fig. S4 Raman of catalysts (a) MoO₃ (b) V₂O₅ (c) Mo-V (d) Mo-V-Te (e) Mo-V-Te-Cs (f) Mo-V-Te-Ti.

Table S1 Integral area after fitting of NH₃-TPD peaks and isobutene oxidation capacity

| Samples | Integral area sum of weakly acidic sites | Integral area sum of moderately acidic sites | Integral area sum of strongly acidic sites | <i>i</i> -C ₄ H ₈ Conversion/% | MAL Selectivity/% | MAA Selectivity/% |
|------------|--|--|--|--|-------------------|-------------------|
| Mo-V | 29.1 | 20.0 | 50.9 | 93 | 28 | 35 |
| Mo-V-Te | 32.1 | 39.5 | 28.4 | 96 | 43 | 39 |
| Mo-V-Te-Cs | 28.5 | 51.5 | 20.0 | 92 | 20 | 71 |
| Mo-V-Te-Ti | 34.0 | 45.0 | 21.0 | 98 | 29 | 62 |
| Mo-V-Te-Ce | 56.0 | 22.4 | 21.6 | 95 | 82 | 10 |

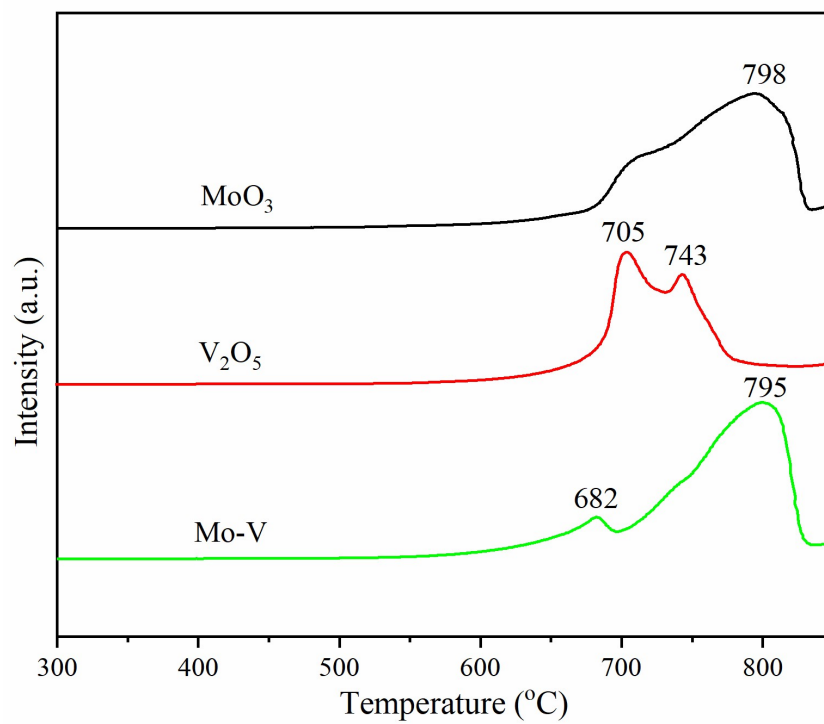


Fig. S5 H₂-TPR profiles of MoO₃, V₂O₅, and Mo-V.