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Supplementary information

Highly Selective Production of Linear 1-Heptadecene from Stearic Acid over a Partially Reduced MoO_x Catalyst

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Experimental Section

Materials

Acetone (99.5%) and Acetic anhydride (Ac_2O, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Bis(2-diphenylphosphinophenyl)ether (DPEphos) was obtained from Sigma-Aldrich, USA. Ammonium molybdate (99.9%) was purchased from the Aladdin Industrial Corporation, China. Stearic acid was purchased from Mecklin Co., China. 1-heptadecene (99.5%) was acquired from TCI (Shanghai) Development Co., Ltd. All reagents were directly used without purification.

Synthesis of MoO_3 and MoO_x-T

A certain amount of ammonium molybdate was heated in a muffle furnace at 500 °C for 4 h to obtain MoO_3 as the catalyst precursor. The as-synthesized MoO_3 was then reduced in an H_2 environment at different temperatures (150, 300, 450, 600, 700 °C) for 2 h to obtain MoO_x-T catalysts, where T represents the reduction temperature.

Experimental procedures and analytical method

In a typical experimental process, a certain amount of stearic acid and MoO_x catalysts together with 30 mg DPEphos and 30 μL Ac_2O were in turns loaded into an 8 mL batch reactor and sealed properly. The sealed reactor was purged three times with nitrogen gas to remove unwanted air molecules and then filled with N_2 at atmospheric pressure. Thereafter, the reactor was heated at the required temperature for a certain amount of time. At the end of the reaction time, the products were recovered from the reactor after quenching in a cold-water bath and subsequently washed in acetone in readiness for GC analysis. The liquid products were analyzed on a gas chromatograph (Agilent 7890B) equipped with an

Agilent CP-FFAP CB capillary column and a flame ionization detector (FID). The gaseous products were analyzed on SHIMADZU GC-2018 gas chromatograph equipped with an Agilent PLOT 5A molecular sieve filled column and thermal conductivity detector (TCD). The identification of the products was done by matching the retention times of the unknown compounds to those of reference standards. The quantitative analysis was performed using external calibration curves for each compound. The conversion of stearic acid and yields of products were calculated using the equations below. The selectivity to 1-heptadecene is determined by dividing moles of achieved 1-heptadecene by moles of generated heptadecene. The reported data are average values of three independent experiments. The calculated conversion and yields of products were all based on the equivalent amount of carbon. The error bars represent the standard deviation of three replicate experiments.

$$\text{Conversion}(\%) = 1 - \frac{\text{moles of remaining reactant}}{\text{moles of reactant added}} \times 100\%$$

$$\text{Yield}(\%) = \frac{\text{moles of product}}{\text{moles of reactant added}} \times 100\%$$

Characterizations

The crystal structure of our MoO_x catalysts was studied by the PXRD technique recorded on PANalytical Empyrean 200895 diffractometer with a Cu Kα source operated at 40 kV and 40 mA. The catalysts scanned over a 2θ range of 10-90°. The temperature-programmed reduction (H_2-TPR) analysis was performed on the FineSorb-3010 instrument equipped with a TCD (Zhejiang Finetec Instruments Co., Ltd.). For the H_2-TPR measurement, the samples were first pretreated at 120 °C for 1 h under Ar flow (rate = 15 mL/min) and then cooled to 60 °C. Following this, the reactor was heated to 800 °C in 10% H_2/Ar flow (30 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The H_2-TPR profiles were acquired after maintaining the temperature at 800 °C for 30 mins. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were both acquired on the JEM-2100 microscopy instrument. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 spectrometer.

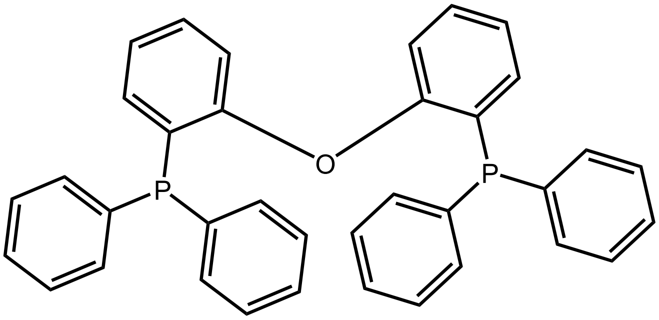

Figure S1. The molecular structure of DPEphos.

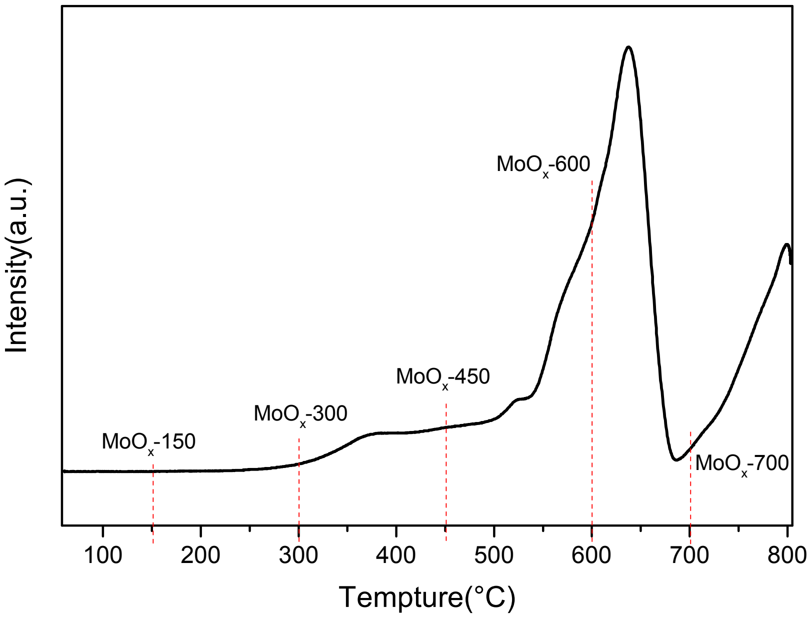

Figure S2. H_2-TPR profile of MoO_3 sample obtained from the calcination of ammonium molybdate at 500 °C.

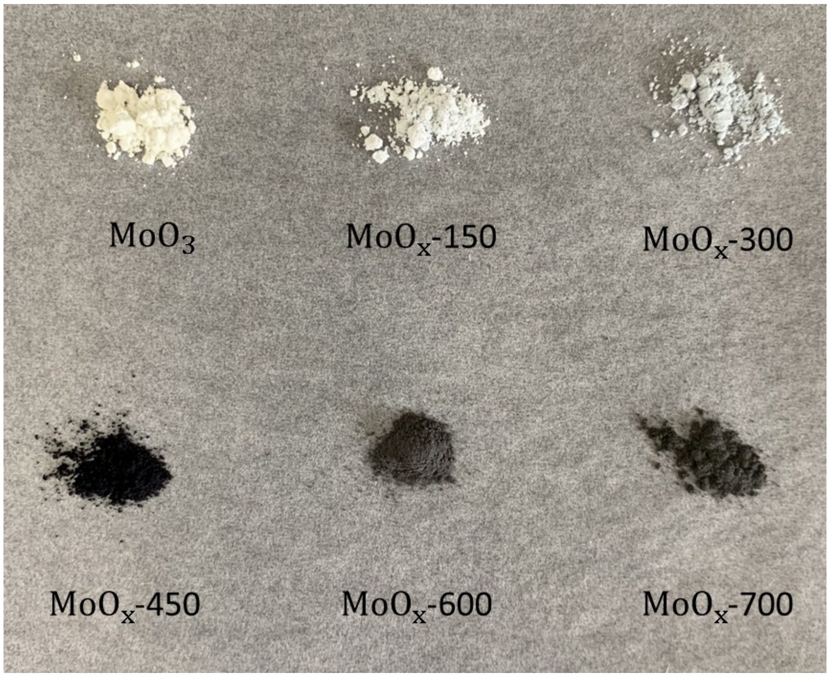

Figure S3. The appearance of MoO_3, MoO_x-150, MoO_x-300, MoO_x-450, MoO_x-600 and MoO_x-700 samples.

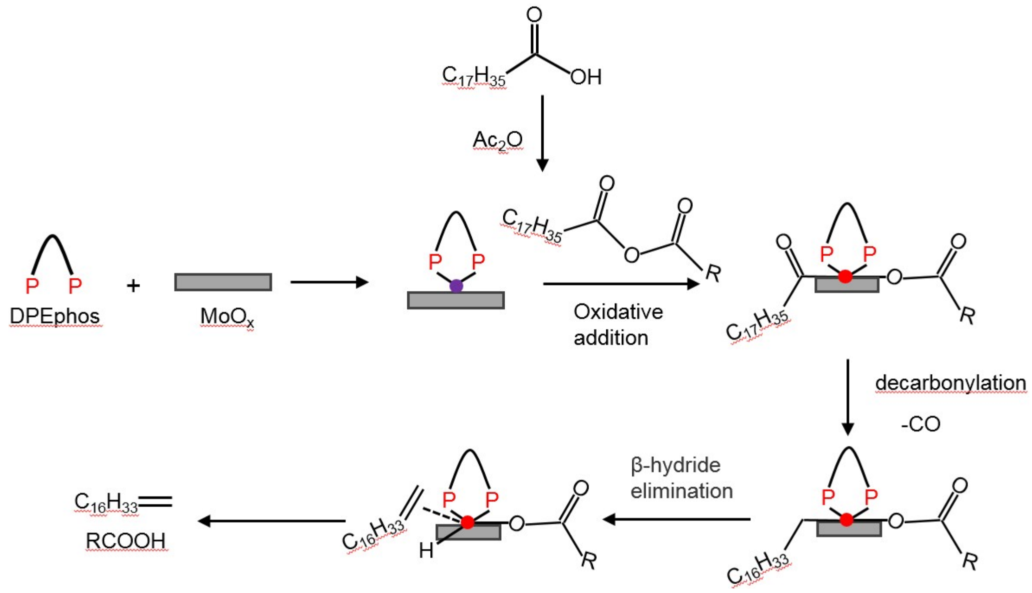

Figure S4. The reaction steps of decarbonylative dehydration of stearic acid in the DPEphos-AcO_2 system.

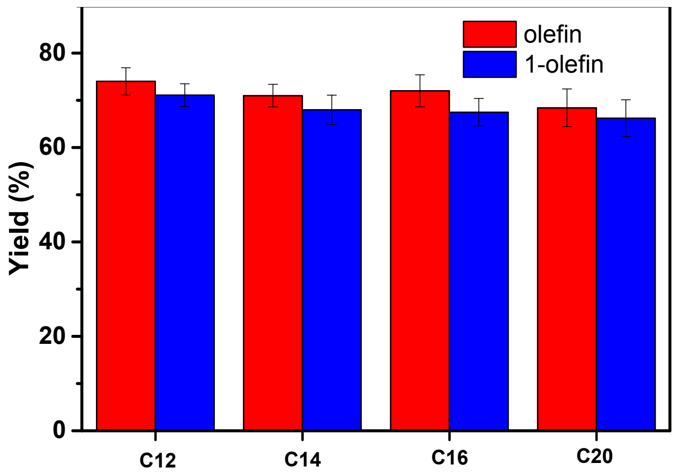

Figure S5. The yield of olefin and 1-olefin from conversion of lauric acid, myristic acid, palmitic acid and eicosanoic acid over MoO_x-600 catalyst; Reaction conditions: Reactant = 50 mg, catalyst = 30 mg, T= 190 °C, t = 16 h, Ac_2O = 30 μL, DPEphos = 30 mg.

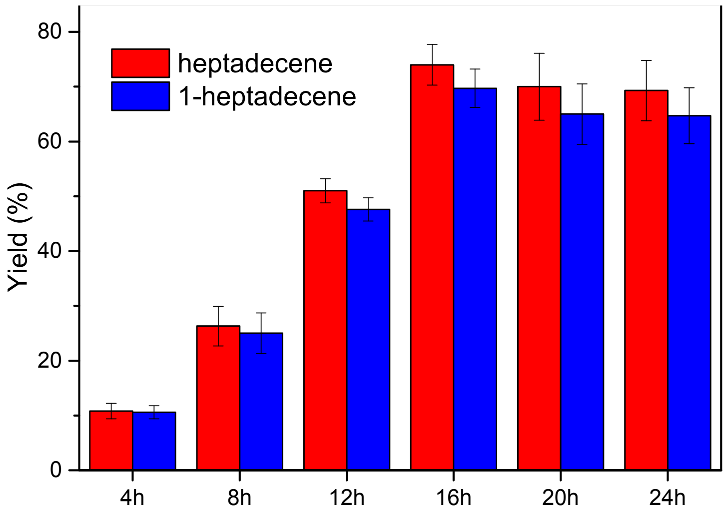

Figure S6. The yield of heptadecene and 1-heptadecene from conversion of stearic acid over MoO_x-600 catalyst with different reaction time; Reaction conditions: Stearic acid = 50 mg, catalyst = 30 mg, T= 190 °C, t = 4~24 h, Ac_2O = 30 μL, DPEphos = 30 mg.

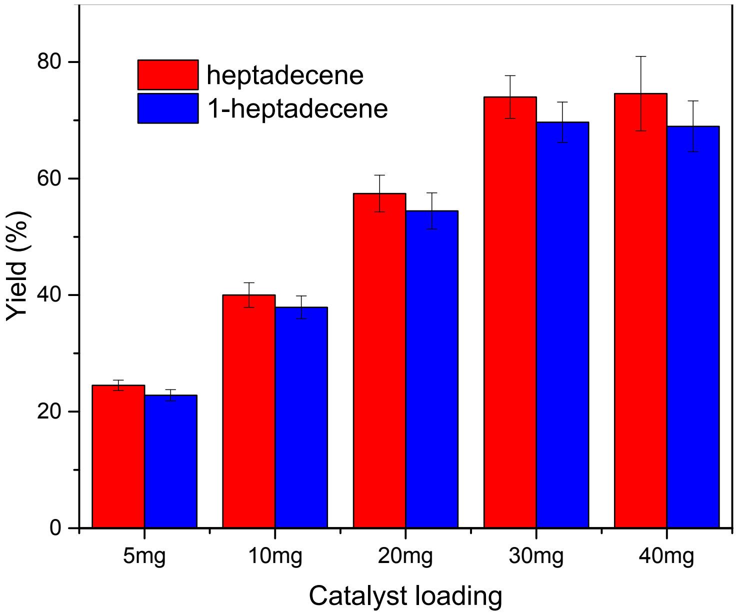

Figure S7. The yield of heptadecene and 1-heptadecene from conversion of stearic acid over MoO_x-600 catalyst with different catalyst loading; Reaction conditions: Stearic acid = 50 mg, catalyst = 5~40 mg, T= 190 °C, t = 16 h, Ac_2O = 30 μL, DPEphos = 30 mg.

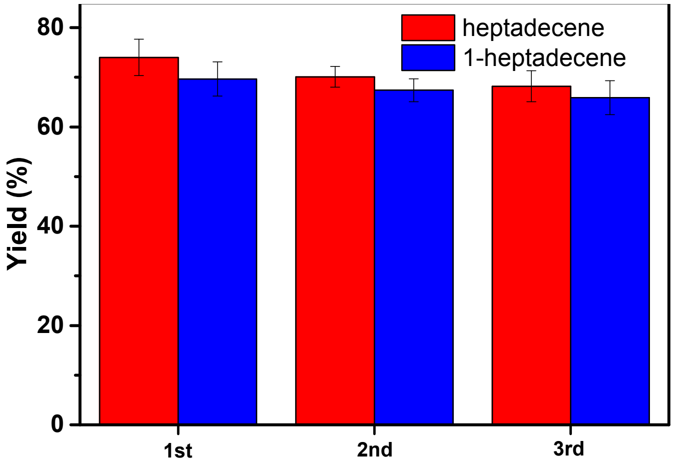

Figure S8. The yield of heptadecene and 1-heptadecene from conversion of stearic acid over fresh (1st), used once (2rd) and used twice (3rd) MoO_x-600 catalysts; Reaction conditions: Stearic acid = 50 mg, catalyst = 30 mg, T= 190 °C, t = 16 h, Ac_2O = 30 μL, DPEphos = 30 mg.

Table S1. XPS binding energy values for Mo $3d_{5/2}$ ($3d_{3/2}$) of MoO_x-450, MoO_x-600, and MoO_x-700 samples

Samples	Mo^0	Mo^{4+}	Mo^{5+}	Mo^{6+}
MoO_x-450	~	228.8 (232.8)	231.0 (234.2)	232.2 (235.5)
MoO_x-600	227.6 (230.8)	228.8 (232.8)	231.2 (234.4)	232.1 (235.5)
MoO_x-700	227.6 (230.7)	228.6 (232.7)	231.3 (234.5)	~