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

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Here, MoO_x -T was developed by a simple reduction of MoO_3 precursors at different temperatures. Interestingly, partially reduced MoO_x -600 obtained by reducing MoO_3 precursor at 600 °C, shows the co-existence of a mixture of different valence states (0, +4, ~+6) of Mo, and as a result, provides a superior catalytic activity.

Linear α -olefins (LAOs) with a terminal C=C double bond are important building blocks for the manufacture of a variety of different value-added chemicals, such as polyolefins, detergents, lubricants, plasticizers, and synthetic oils.1-4 At present, a predominant preparation strategy for the manufacture of LAOs involves the oligomerization of ethylene derived mostly from petroleum resources. This production strategy, however, has three main limitations: 1) the ethylene feedstock is mainly derived from fossil resources; 2) control growth of the carbon chain length to obtain products with a single carbon chain length is a difficult task to accomplish, and 3) the as-obtained LAOs are certainly of even-chain length.5-7 Biomass-derived fatty acids abound in low-cost waste cooking oils and animal fats which can be converted to valuable hydrocarbons, including LAOs by mere deoxygenation.⁸⁻¹⁰ This deoxygenation of fatty acids has been identified as a complementary strategy to oligomerization of ethylene and can be used to obtain odd-chain LAOs from even-chain fatty acids.1 This unique complimentary strategy is not limited by the above-mentioned challenges.¹¹⁻¹³ Different catalytic systems such as heterogeneous, homogeneous, and biocatalysis have been investigated for the selective transformation of fatty acids to LAOs. However, the

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The side reactions, such as isomerization and decarboxylation to saturated alkanes, is perhaps the most important factor limiting high selectivity to LAO production in heterogeneous systems. For example, Lopez-Ruiz and coworkers studied decarbonylation of heptanoic acid using Pt/C and Pd/C catalysts, and achieved a relatively high α -selectivity of 57% over the gas-phase operations but < 15% α -selectivity in the liquid-phase operations (Scheme 1).^{16, 17} Although > 90% selectivity to LAO production has been reported over a Lewis-acid gamma-Al₂O₃ or WO_x-Al₂O₃ catalyst, the reactants, however, are only limited to unsaturated fatty acids.¹⁸ To overcome these challenges, a very recent study from Jensen and co-workers employed a commercial Pd/C catalyst (Scheme 1), through optimized phosphine ligand - DPEphos (molecular structure shown in Fig. S1, ESI⁺) mediated strategy, and achieved high selectivity to LAO production from saturated fatty acids conversion.¹² Considering the high cost of noble metal - Pd catalyst, the development of rather cost-effective, non-noble metal-based, heterogeneous catalyst for highly selective production of LAOs from fatty acid conversion, is highly desirable from economic standpoint.



b This work: non-noble-metal MoO_x catalysts





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In the present study, therefore, we developed for the first time, a partially reduced, non-noble metal oxide-based (MoO_x) catalyst for highly efficient and selective production of 1-heptadecene through decarbonylative dehydration of stearic acid in the presence of Ac₂O and phosphine ligands. The reduction temperature of the MoO₃ precursor was found to have a profound influence on the catalytic activity of the resultant MoOx-T-based catalyst for the production of both heptadecene and 1-heptadecene. A series of characterization techniques including the powder X-ray diffraction (PXRD), temperature-programmed reduction measurements, highresolution transmission electron microscopy (HR-TEM), and X-ray photoelectron spectroscopy (XPS), were used to investigate the structure, composition, surface and bulk chemical properties of the MoO_x-T catalysts. Through the variation of different reaction times and the mass of catalyst added, the catalytic performance of our partially reduced MoO_x-T catalyst was optimized for the production of both heptadecene and 1-heptadecene.

To understand the influence of reduction temperature on the crystal structure of the as-synthesized MoO_x-T, the X-ray diffraction (XRD) patterns of the catalysts were recorded and are shown in Fig. 1. The XRD pattern of MoO_x (obtained from the calcination of ammonium molybdate at 500 °C) shows the characteristic peaks of MoO₃ (PDF #05-0508) before reduction. Upon exposure of MoO_x to H₂ reducing environment at 150 °C (MoO_x-150) and 300 °C (MoO_x-300), the diffraction patterns of MoO_x-150 and MoO_x-300 both very closely resemble that of unreduced MoO_x , indicating that MoO_3 reduction is quite difficult to accomplish at a temperature below 300 °C. The temperature-programmed reduction (H₂-TPR) analysis profile of MoO_{3.} which has no H₂ consumption peak below 300 °C (Fig. S2, ESI+) additionally collaborates this claim. As the reduction temperature was increased to 450 °C (MoO_x-450), the characteristic MoO₂ diffraction peaks (PDF #32-0671) appeared at the expense of the peak intensity of MoO₃. The occurrence of new diffraction peaks at approximate 2θ value of 22.5° is attributed to the formation of a small amount of Mo_4O_{11} (with Mo valence between +4 and +6), as consistent with the previous report.¹⁹ Upon further increase of the reduction temperature to 600 °C (MoO_x-600), the diffraction peaks of MoO₃ disappeared completely as characteristic diffraction peaks of both MoO₂ and Mo emerged, showing a complete reduction of bulk MoO₃ precursor at 600 °C.



Fig. 1 XRD patterns of the MoO_3 and MoO_x -T catalysts; Reference: Mo (orange), MoO_2 (pink), and MoO_3 (black).



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Fig. 2 TEM images of the (a) MoO_3 , (c) MoO_x -600, and (e) MoO_x -700 samples and their corresponding HRTEM images (b, d, and f).

The XRD pattern of the sample following a reduction in the H_2 environment at 700 °C (MoO_x-700) contains the characteristic peaks of a metallic Mo (PDF #42-1120). The physical appearance of all six samples (MoO₃, MoO_x-150, MoO_x-300, MoO_x-450, MoO_x-600, and MoO_x-700) during these transition stages was noted and is presented (Fig. S3, ESI⁺).

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of MoO₃, MoO_x-600, and MoO_x-700 are shown in Fig. 2. The TEM image of MoO₃ (Fig. 2a) shows a portion of striplike particles, which are invisible in the MoO_x-600 and MoO_x-700 samples. Notably, all three samples are composed of a disorderly accumulation of granular compounds. The HRTEM image of MoO₃ shown in Fig. 2b shows the distinct (110) lattice planes of MoO₃ with lattice spacings of 3.7 Å. For the MoO_x-600 sample, the lattice planes ascribed to Mo (110) and MoO₂ (-111) with the lattice spacings of 2.3 Å and 3.5 Å, respectively, co-exist, suggesting the partial reduction of Mo⁶⁺ in its bulk phase. The HRTEM image of MoO_x-700 (Fig. 2f) has only the metallic Mo lattice planes, which indicates a fairly complete reduction of all suboxide intermediates in the bulk phase. This observation is consistent with the XRD results.

Whereas XRD and TEM results provide comprehensive insights into the composition of MoO_x catalysts in the bulk phase, the surface composition and chemical state of a catalyst usually have more direct and profound influence on its catalytic activity, hence, the X-ray photoelectron spectroscopy (XPS) (high-resolution) of Mo 3d was used to investigate the surface properties of our MoO_x catalysts, as shown in Fig. 3. For the MoO₃, MoO_x-150, and MoO_x-300 catalysts (Fig. 3a-3c), two obvious characteristic peaks from 3d 5/2 and 3d 3/2 are located at 232.5 and 235.7 eV, respectively, suggesting the sole existence of Mo⁶⁺ species on the catalyst surface.²⁰ It should be Published on 11 March 2020. Downloaded on 3/12/2020 1:20:27 AM

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Fig. 3 High-resolution XPS spectra of Mo 3d in (a) MOO_3 , (b) MOO_x -150, (c) MOO_x -300, (d) MOO_x -450, (e) MOO_x -600, and (f) MOO_x -700 samples.

recalled that the lone existence of Mo⁶⁺ species on these catalysts was equally reported for the material bulk (XRD results) since the reduction temperatures (≤ 300 °C) are quite insufficient to induce partial reduction. For the MoO_x-450 catalyst, the deconvoluted peaks in Fig. 3d unambiguously revealed the co-existence of Mo⁴⁺, Mo⁵⁺, and Mo^{6+ .^{21, 22} The surface state of the MoO_x -450 catalyst is similar to that in the bulk phase since the peaks ascribed to MoO_2 , Mo_4O_{11} , and MoO₃ were equally observed in the XRD pattern. The XPS spectrum of MoO_x-600 (Fig. 3e) has new peaks at 227.6 eV and 230.8 eV, that suggests the existence of molybdenum in zero oxidation state (Mo⁰). Although MoO₂ and Mo crystalline phases are both present in the MoO_x -600 catalyst, the Mo phase with a valence state above +4 is only visible in the XPS profile and not the XRD pattern. This observation indicates that the surface composition of MoO_x-600 has a wide distribution of Mo in 0, +4 and/or ~+6 valence states. For the MoO_x-700 sample, the disappearance of Mo⁶⁺ species was observed in the XPS profile, with increased production of Mo⁰ (Fig. 3f). The XPS binding energy values of different Mo valence in MoO_x-450, MoO_x-600, and MoO_x-700 are summarized in Table. S1. In both MoO_x -600 and MoO_x -700 samples, the difference in the oxidation state of Mo on the catalyst surface relative to the bulk phase, is possibly due to the relative instability of MoO_x on the surface containing a lower Mo valency. Overall, the distribution of various Mo species can be controllably tuned by different reduction temperature.



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Fig. 4 Yields of heptadecene and 1-heptadecene from conversion of stearic acid over the MoO_x -T catalysts; Reaction conditions: Stearic acid = 50 mg, catalyst = 30 mg, T= 190 °C, t = 16 h, Ac₂O = 30 µL, DPEphos = 30 mg.

Biomass conversion is an efficient route to produce the renwable biofuel and value-added chemicals.²³⁻²⁵ In this work, a series of MoO_x-T-based catalytic system was investigated for decarbonylative dehydration of stearic acid at 190 °C for 16 h in the presence of DPEphos (Fig. S1, ESI⁺) and acetic anhydride (Ac₂O). The detailed reaction conditions are summarized in Fig. 4. This DPEphos and Ac₂Oassisted catalytic system was first reported by Jensen and coworkers, who utilized a commercial, heterogeneous Pd/C catalyst to achieve an α -olefins yield above 70%.¹² In DPEphos-AcO₂ catalytic system, the catalyst with attached DPEphos ligand can react with anhydride obtained from the conversion of stearic acid and Ac₂O to produce acyl carboxylate. Subsequent decarbonylation and βhydride elimination of the acyl carboxylate proceed to obtain 1heptadecene. The reaction steps are shown in Fig. S4.12 In the present MoO_x catalytic system, the significant influence of reduction temperature on catalytic performance towards decarbonylative dehydration of stearic acid is clearly visible in Fig. 4. For the nonreduced catalysts (MoO₃, MoO_x-150, and MoO_x-300), both the yields of heptadecene and 1-heptadecene were below 18% (the yield of heptadecene/1-heptadecene was calculated by dividing the moles of heptadecene/1-heptadecene recovered by the initial moles of stearic acid). We then investigate the uncatalyzed stearic acid conversion of stearic acid and obtained yields of 1-heptadecene is only ~16%. However, an increase in the yield of heptadecene from 17.4% to 33.2% was observed upon increasing the reduction from 300 °C to 450 °C. This improvement in catalytic performance can be attributed to the formation of a small amount of under-coordinated Mo (Mo⁴⁺ and Mo⁵⁺) in MoO_x-450 resulting from the removal of oxygen. This implies that the formation of under-coordinated Mo4+ and Mo⁵⁺ accelerates decarbonylative dehydration of stearic acid. Interestingly, the yield of heptadecene increased significantly up to 74.0% in MoO_x-600 catalyst with selectivity to 1-heptadecene as high as 95%. The carbon balance is same as the yield of heptadecene since the product obtained from the reaction of stearic acid and Ac₂O can not be detected with gas chromatography. The MoO_x-700 catalyst, on the other hand, afforded a relatively lower yield of heptadecene as compared to MoO_x-600, which indicates that excessive reduction of the MoO₃ precursor is equally detrimental to heptadecene production. In addition to stearic acid, MoOx-600 catalyst also displays the comparable catalytic performance for the conversion of

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lauric acid, myristic acid, palmitic acid and eicosanoic acid with different carbon numbers (Fig. S5, ESI⁺).

Further, the stearic acid conversion was studied over a range of reaction times (4 h, 8 h, 12 h, 16 h, 20 h, and 24 h) at 190 °C to determine the optimum reaction time. As seen in Fig. S4, ESI⁺, the obtained yields of heptadecene progressively increased from 4 h to 16 h of reaction times (Fig. S6, ESI⁺). Further increase in the reaction time beyond 16 h resulted in no additional increase in the yield of heptadecene, revealing that 16 h of reaction time was enough for maximum utilization of stearic acid. The effect of the mass of the catalyst added on heptadecene was equally investigated through variation of the catalyst amount from 0 - 40 mg. Among the different masses of the catalyst investigated, the 30 mg of MoO_x-600 catalyst was found to be the most ideal concentration (Fig. S7, ESI⁺). By introducing DPEphos and Ac₂O into the heterogeneous catalytic system, high selectivity to 1-heptadecene can be guaranteed over different catalysts under different reaction conditions. It should be noted that that inability of the yield of 1-heptadecene to increase beyond 70% despite the prolonged reaction time and optimized mass of the catalyst added, is mainly due to the formation of highly concentrated unsaturated olefins (near 70% yield) and decarbonated product CO, which occludes the catalyst pores and poisons the active sites, as previously reported.¹² More importantly, the MoO_x-600 catalyst can be reused for at least three times without the significant loss of catalytic activity (Fig. S8, ESI⁺).

Summarily, a partially reduced MoO_x-600 catalyst that shows the co-existence of different Mo species (0, +4 ~+6) was successfully developed and investigated for decarbonylative dehydration of stearic acid. This catalyst exhibited an outstanding catalytic performance toward decarbonylative dehydration of stearic acid and achieved a yield of heptadecene close to 75.0% with selectivity to 1-heptadecene production close 95%. Notably, the catalytic activity of this partially reduced MoO_x-600 catalyst is higher than that of the non-reduced MoO₃ and over-reduced MoO_x-700 catalysts, making it suitable for the production of linear α -olefins from biomass-derived fatty acids.

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Conflicts of interest

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There are no conflicts to declare.

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