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Continuous synthesis of molybdenum oxide microspheres by ultrasonic spray pyrolysis

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ABSTRACT

Molybdenum oxides microspheres with prominent MoO₂ phase were produced successfully by ultrasonic spray pyrolysis under reducing conditions. Ethylene glycol addition in the precursor solution was found to promote complete truncation of regular molybdenum oxides particle geometry into rectified spherical micro particles during spray pyrolysis. It also removed the MoO₃ and Mo₄O₁₁ phases, while maintaining nanocrystalline MoO₂ phase structure. However, addition of EG reduced the surface area and increased the pore size rather significantly, which might adversely affect the catalytic performance of MoO₂ microspheres. Catalytic activity of the product molybdenum oxides was investigated for partial oxidation of *n*-dodecane.

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Introduction

The road map on the use of hydrogen (H₂) to propel hydrogen economy in Japan was announced in 2014 [1]. Following this announcement, Tokyo has earmarked \$350 million to subsidize and invest H₂ fuel cell cars and infrastructure such as H₂ fueling stations. The investment also includes 6000-unit Olympic village that functions exclusively on fuel cell power to initiate a transition to hydrogen powered society [2]. Although H₂ has been used as fuel to power rocket for decades, its application in commercial vehicles has not been materialized due to problem of storage and other issues related to H₂ production. There are many ways to produce H₂, among them include electrolysis, thermolysis, biomass gasification, bio-catalysis or fermentative hydrogen production. However, the most economically feasible technology for producing H₂ is still from fossil sources such as in a steam reforming of hydrocarbons and partial oxidation of paraffin.

In the partial oxidation of a paraffin namely *n*-dodecane to produce H₂, molybdenum oxide has been chosen as an active catalyst. Molybdenum oxide has also been extensively used in an

area such as hydrocarbon decomposition [3,4] and it has been used as anode materials in fuel cells and lithium-ion batteries [5] because of its high catalytic activity, sulfur tolerance and high electrical conductivity [5,6]. Despite these advantages, commercial molybdenum oxide exhibits low surface area of 0.29 m²/g. High active surface area is needed in order to achieve high catalytic performance. Higher surface area of 48 m²/g was successfully achieved previously by a solvothermal method [7]. Attempts to improve the surface area in order to increase the H₂ yield to a higher level is expected to continue in the future.

Besides high surface area, there is also a need to synthesize molybdenum oxide that exhibits high purity, uniformity, strength, and chemical durability to produce hydrogen at extreme conditions. In order to achieve this quality, molybdenum oxide that consists predominately of MoO₂ phase should be obtained. MoO₂ is industrially produced from reduction of MoO₃ by H₂ at temperature between 450 °C and 600 °C [8], and through redox reaction between Mo₂O₇²⁻ and NH₂C₆H₄NH₂ at low temperature [9]. Thus, a proper synthesis procedure and system should be made available to prevent the oxidation from taking place and to obtain a stable MoO₂ particle with a proper geometry. MoO₂ particle could exhibit a different geometry such as microsphere [9] and nanostructure [10]. MoO₂ could also be formed into other geometrical shapes such as nanoplate or nanosheets [10] and nanostars [11]. In this study, we synthesized MoO₂ microspheres by continuous ultrasonic spray pyrolysis under reducing conditions. The resulting particles were used as catalysts in partial oxidation of *n*-dodecane.

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Material and methods

Molybdenum oxides synthesis by continuous spray pyrolysis

Ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 81–83%, Aldrich), used as the metal precursor, was first dissolved in de-ionized (DI) water to make the precursor concentration of 0.1 M. In order to investigate the effect of ethylene glycol (EG), the solvent was changed to the mixture of EG and DI water at the volume ratio of 1 with the same precursor concentration of 0.1 M. The solution was placed in an ultrasonic nebulizer of a continuous ultrasonic spray pyrolysis system such as shown in Fig. 1 [12]. The spray pyrolysis system utilized in this work consists of a spraying zone, a heating zone, and a powder collecting zone all in a continuum. The main component in the spraying zone is the ultrasonic nebulizer (1.7 MHz) having six vibrators to generate extremely fine droplets. The nebulous droplets were carried into the heating zone by a carrier gas which was a gas mixture of nitrogen and hydrogen. Hydrogen was introduced to serve as a reducing agent and to activate the fine molybdenum oxide particles. In this work, a binary gas mixture consisting of 33 vol% or 66 vol% of H₂ in N₂ was used to achieve the above purposes. The droplets were then induced through a 900 mm length of quartz reactor at a fixed temperature of 600 °C for 2 s in the heating zone. The pyrolyzed particles were collected from the collecting zone with a Teflon filter. The product molybdenum oxides were labeled as sample A, and sample B, depending on preparation conditions such as shown in Table 1. Commercial molybdenum oxide particles (Aldrich, 99% MoO₂) with density of 6.47 g/mL were used in a comparative analysis with the samples prepared from this work.

Characterization of molybdenum oxides

X-ray diffraction patterns were obtained using XRD equipment (XRD; MAC-18XHF, Rigaku, Japan) to identify the crystal phases of the collected samples at narrow angle from 20° to 80° using nickel

filtered Cu K α radiation ($k = 1.5406 \text{ \AA}$), with accelerating voltage and current of 40 kV and 40 mA, respectively. Nitrogen adsorption was performed using a volumetric gas-sorption system (ASAP 2020, Micrometrics, USA) to analyze BET surface area, pore size, and pore volume. The morphology and textural details of the samples were observed by a field-emission scanning electron microscope (FE-SEM; Leo-Supra 55, Carl Zeiss STM, Germany). Thermogravimetric analyzer (TGA; Q50, TA Instrument, USA) was performed at a rate of 2 °C/min under N₂ and H₂ environment.

Catalytic activity of molybdenum oxides in partial oxidation of *n*-dodecane

The molybdenum oxide spherical catalysts collected from the system were placed in a quartz reactor. It was sandwiched between two layers of quartz wool to maintain the bed position and prevent the catalysts from flowing out of the reactor together with the gaseous products. While *n*-dodecane (C₁₂H₂₆) was vaporized at 450 °C and 0.5 mL/h, a binary mixed gas consisting of 79.5 vol% argon and 20.5 vol% oxygen, serving as an oxidizing agent, was introduced in the pre-heater. The mixed gas containing oxygen to carbon ratio at 0.7 was fed into the reactor at weight-hourly-space-velocity (WHSV) of 6.4 h⁻¹ following the method reported in the literature [7]. After being separated from the un-reacted *n*-dodecane, water, and other condensable products at 4 °C, the gaseous products were monitored using gas chromatograph (GC-17A, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD). The catalytic activity was calculated in terms of C conversion based on the stoichiometric atoms in the *n*-dodecane,

$$C \text{ conversion} = \frac{n_{\text{CH}_4}^{\text{out}} + n_{\text{CO}}^{\text{out}} + n_{\text{CO}_2}^{\text{out}}}{12 \cdot n_{\text{C}_{12}\text{H}_{26}}^{\text{in}}} \quad (1)$$

where $n_{\text{C}_{12}\text{H}_{26}}^{\text{in}}$ is the number of mol of *n*-dodecane in the feed and $n_{\text{CH}_4}^{\text{out}}$, $n_{\text{CO}}^{\text{out}}$ and $n_{\text{CO}_2}^{\text{out}}$ are the number of mol of methane, carbon monoxide and carbon dioxide in the product stream, respectively.

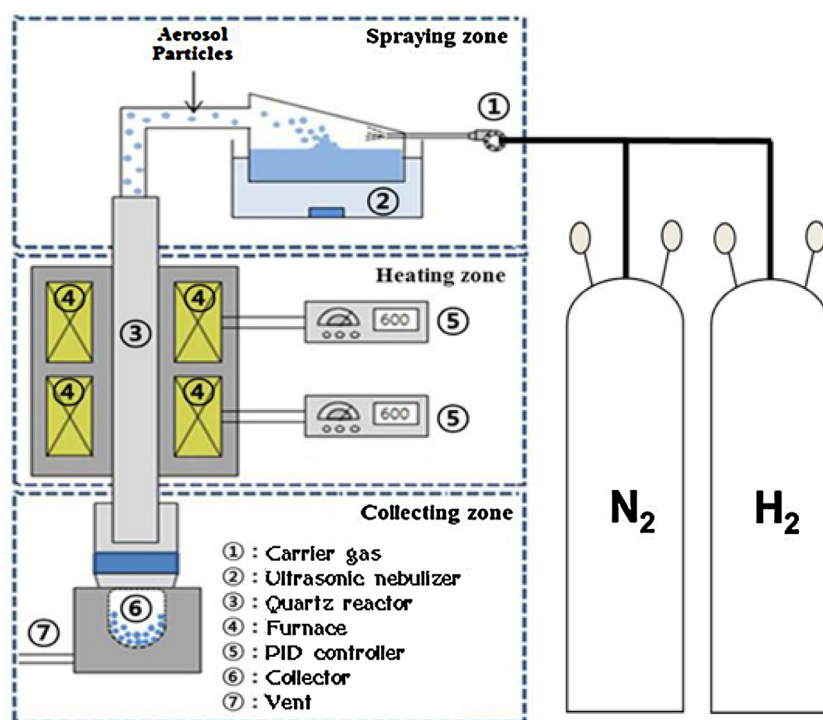


Fig. 1. Schematic diagram of a continuous ultrasonic spray pyrolysis system.

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