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Facile synthesis of $Mo/Al_2O_3–TiO_2$ catalysts using spray pyrolysis and their catalytic activity for hydrodeoxygenation

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ABSTRACT

In this study, spherical mixed oxides of Al_2O_3 and TiO_2 supported molybdenum (Mo) catalysts, $Mo/Al_2O_3-TiO_2$, were successfully prepared using a novel approach combining sol-gel and spray pyrolysis (SP) methods. First, both boehmite sol and titania sol were prepared by a sol-gel process, and then molybdate salt was dispersed in the sol mixture with the assistance of citric acid, followed by spray pyrolysis of the mixed precursor solution. Structural analyses of prepared catalysts showed that the dispersion of active sites was affected by the TiO_2 concentration in the $Al_2O_3-TiO_2$ mixed oxide support. The catalytic activities of reduced catalysts were investigated for hydrodeoxygenation (HDO) of palmitic acid, which is the main component of microalgae–derived biocrude. The results show that the $Mo/Al_2O_3–TiO_2$ catalysts exhibited excellent catalytic performance for the HDO of palmitic acid.

1. Introduction

Bio-oils obtained from pyrolysis or hydrothermal liquefaction of biomass usually contain significant quantities of several oxygen-containing compounds such as organic acids, aldehydes, ketones, and phenolic compounds [1,2]. The high oxygen content in biocrude composition can cause high acidity, high viscosity, low heating value, instability, and immiscibility with hydrocarbon fuels, which results in poor bio-oil quality [3]. Therefore, various methods for upgrading the quality of biomass–derived biocrude have been studied to find an effective solution for transportation fuels. Among them, the hydrogedeoxyenation (HDO) reaction is one of the most potentially valuable processing routes to selectively cleave C—O and C—C bonds in oxygen–containing compounds [4].

There have been many types of HDO catalysts with various support and dopant materials reported in recent years. Faba et al. [5] investigated the HDO of acetone-furfural over Al_2O_3-supported noble metal (Ru, Rh, Pd, and Pt) catalysts. Nguyen et al. [6] studied the HDO of guaiacol over noble metal-based catalysts (Au, Rh, AuRh) supported on TiO_2. They reported that the product selectivity depended on the metal dopant species and reaction temperature. It is well-known that the exorbitant price of these noble metal-based catalysts may hinder their application on larger scales [7,8]. Therefore, the development of non-noble metal catalysts for HDO reaction has been thoroughly investigated by many researchers. In recent years, Co, Ni, and Mo-based catalysts have been studied extensively. These metals can be used as monometallic dopants (Co, Ni, Mo, etc.) or bimetallic dopants (NiMo, CoMo, etc.) on various catalyst supports for HDO [9–11]. Also, catalysts of metal phosphides [12–16] or metal sulfide systems [10,17,18] have attracted tremendous attention due to their excellent properties in HDO. However, these catalysts have disadvantages such as final products contamination due to dissolving of sulfur into reactants, water-evoked catalyst deactivation and coke formation [8]. For metal–based catalysts, support plays a very important role in catalytic reactions since characteristics such as surface area and pore size strongly affect the mass transfer of the reactants. Besides, the interaction between the support and metal dopant is a very important factor that could facilitate or inhibit the activity of catalysts [7,19–23]. Very recently, De Souza et al. [24] investigated the effects of support materials (SiO_2, TiO_2, Al_2O_3, ZrO_2, CeO_2 and $CeZrO_2$) on the performance of Pd-based catalysts for the HDO of phenol. They found that product distribution is significantly affected by support materials. In addition to this, the catalytic stability was also affected by the species of the support materials [24]. The composite supports, including binary oxides of γ-Al_2O_3 mixed with TiO_2, ZrO_2, and SiO_2, showed promising properties in catalysis processes [19,25–29]. The modification of Al_2O_3 by TiO_2 was found to

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improve catalytic properties such as higher reducibility and better dispersion of metal dopant species compared with pure Al_2O_3 or TiO_2, providing more active sites for catalysts [26,30]. Some researchers reported that the Al_2O_3–TiO_2 composite supported catalysts showed higher catalytic activities compared to pure Al_2O_3 supported ones [29,31,32]. Tavizón-Pozos [33] found that the use of Al_2O_3–TiO_2 (molar ratio Al/Ti = 2) support for bimetallic CoMo catalyst facilitated dispersion of Mo species in the oxide phase with an octahedral coordination, showed a higher fraction of active sites and improved catalytic activity during HDO. Pophal et al. [34] reported that the hydrodesulfurization (HDS) conversion of 4,6-dimethydibenothiophene over Al_2O_3–TiO_2 supported metal catalysts was much higher than that obtained with only Al_2O_3 support. These results confirm that the binary Al_2O_3–TiO_2 mixed oxide is a promising support material for catalysts.

For doping metal or metal oxide on the support, impregnation, precipitation, and hydrothermal deposition techniques are usually used. Among these approaches, impregnation has been extensively used for preparing catalysts [6,9,24,35,36]. However, there exist two intrinsic disadvantages resulting from the impregnation route: (1) the lack of uniform particle and active species distribution due to the forced condensation of metal precursors on the support surface during the drying process, and (2) limited activity because of the limited amount of active metals deposited on the support surface [35,37]. Liu et al. [35] compared the preparation route of NiMO/Al_2O_3 catalyst for HDS of dibenothiophene and found that the catalyst obtained from the coprecipitation method produced a homogenous distribution of metal sites, while that obtained from the impregnation method caused aggregated metal crystals. It was reported that the catalyst preparation method had a major influence on the physicochemical properties of the catalysts and their activities [23,36]. Therefore, the development of a catalyst preparation route is an important factor that can improve catalytic activity. Besides, a method that is simple and energy-efficient for preparation of a catalyst would be considered a promising strategy for industrial production of catalysts. Recently, spray pyrolysis has attracted tremendous attention because it can produce not only catalysts with high catalytic activity, but also large amounts of catalyst due to its natural continuous flow process [3,38,39]. Ly et al. [3] compared the catalytic activity of Ni, Co, Ni_2P and CoP supported on Al_2O_3 catalysts synthesized using impregnation and a spray pyrolysis method on the HDO of 2–furyl metyl ketone, observing that the catalysts derived from spray pyrolysis had much higher catalytic activities than those derived from impregnation. In fact, a spray pyrolysis method is widely used in industry to produce fine-grained powders (> 0.5 µm) because it is relatively cost-effective and quite versatile [39]. The general mechanism for spray pyrolysis involves four major steps: (1) generation of droplets from precursor solution, (2) shrinkage of droplets due to evaporation, (3) conversion of precursor into oxides, and (4) solid particle formation [38,39].

In this study, the Al_2O_3–TiO_2 binary mixed oxides supported molybdenum catalysts were prepared by a novel method combining sol-gel and spray pyrolysis methods and their catalytic activities for the HDO of palmitic acid were screened. During the spray pyrolysis process, the spherical composite particles were formed directly from the droplets containing a well-dispersed mixture of molybdenum salt, boehmite sol, and titania sol through one–step pyrolysis. The effect of TiO_2 concentration in the Mo/Al_2O_3–TiO_2 catalysts on the HDO of palmitic acid was systematically investigated. Palmitic acid was selected as a bio-oil model compound, as it was found to be a major component (ca. 50%) in the bio-oil obtained from pyrolysis and hydrothermal liquefaction of microalgae *Aurantiochytrium* sp. KRS 101 in our previous studies [1,2]. The catalysts prepared by spray pyrolysis were characterized by XRD, NH_3–TPD, FE-SEM, EDX, FT-IR, XPS, N_2 porosimetry and temperature–programmed reduction (TPR) before their catalytic activities were tested. A series of systematic experiments on the HDO of palmitic acid were conducted to investigate the feasibility of these catalysts for bio-oil upgrading.

2. Experimental

2.1. Catalyst preparation

In this study, Al_2O_3–TiO_2 binary mixed oxides supported molybdenum catalysts were synthesized by combining the sol–gel process and spray pyrolysis method. First, stable boehmite sol (0.1 M) and titania sol (0.1 M) were prepared separately by using the modified Yoldas process [40]. The synthesis procedure of boehmite sol was reported in our previous study [3]. The 0.1 M titania sol was synthesized by hydrolysis and condensation of titanium tetraisopropoxide (TTIP, Ti $(OC_3H_7)_4$, 97%, Aldrich). TTIP was first dissolved in isopropanol at room temperature and a water-free atmosphere. Then, the resulting solution was then added slowly into the desired amount of distilled water under vigorous stirring condition for 2 h, thus white precipitates appeared. The slurry was filtered and washed several times with distilled water to remove alcohol. The obtained precipitates were dispersed in 500 ml of water, followed by peptization with an addition of 1 M HNO_3 solution. The solution was then refluxed at 80 °C for 12 h to obtain a stable sol.

The boehmite sol and titania sol were mixed at various weight ratios of Al_2O_3:TiO_2 = 95:5, 90:10, 80:20, and 70:30 under vigorous stirring for 1 h. A calculated amount of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Aldrich) corresponding to 30 wt% of Mo loading for the catalyst was dissolved in deionized water, followed by adding citric acid (CA, $C_6H_8O_7\cdot H_2O$, 99.0%, Aldrich) to the molar ratio of CA/Mo = 1.2. Citric acid was added to induce the hollow morphology of the product particles during pyrolysis and to increase the surface area of the products [41–43]. The obtained molybdenum solution was added dropwise to the sol mixture while stirring. The resulting mixed solution was then used as precursor solution for spray pyrolysis.

The precursor solution was nebulized by a 1.7 MHz ultrasonic spray generator. The generated droplets were carried into a quartz reactor heated at 600 °C by a constant flow N_2 gas. The produced particles were collected in a Teflon bag installed at the bottom of the spray pyrolysis unit [3]. The schematic diagram of ultrasonic spray pyrolysis is shown in Fig. 1. The obtained samples from spray pyrolysis were then calcined at 500 °C for 3 h with a ramping rate of 2 °C/min in air. These calcined catalysts are denoted as Mo/Al_2O_3, Mo/(95Al − 5Ti), Mo/(90Al − 10Ti), Mo/(80Al − 20Ti), Mo/(70Al − 30Ti), and Mo/TiO_2, depending on the support compositions.

For comparison, 30 wt% Mo-doped Al_2O_3 − TiO_2 catalyst was also prepared by incipient wetness impregnation technique (IM). The

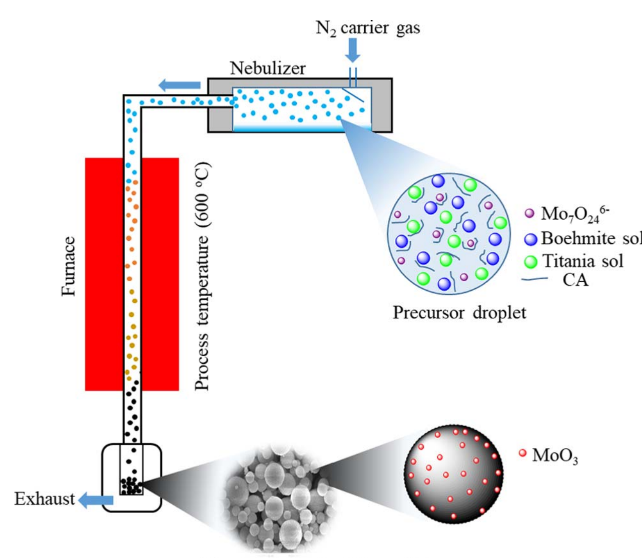

Fig. 1. Schematic diagram of the spray pyrolysis apparatus.