

# Hydrothermal Plant Oil Deoxygenation catalyzed by Pd supported on Mesoporous Silica with *in-situ* Renewable Hydrogen Production

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## Highlights

- H<sub>2</sub>-free catalytic hydrothermal deoxygenation of rapeseed oil was tested at 593 K.
- Isolated APR test reactions were performed to estimate the *in-situ* hydrogen production.
- Pt/MCM-41 shows superior catalytic activity than Pd/SBA-15 and Pd/MCM-41.

## 1. Introduction

The concerns surrounding fossil fuel consumption including reserves depletion, increased demand for industrialization, environmental issues, and macroeconomic factors, present an ongoing serious challenge and thus led to the investigation of more sustainable and renewable alternatives [1,2]. Present studies are directed toward producing “drop-in” fuels, which are found to be a promising synthetic solution for conventional fuels [3]. These are biomass-derived liquid fuels that are in accord with the specifications of petroleum-derived hydrocarbon fuels through solar-driven processes [2,3]. Further, CO<sub>2</sub> generated from biomass can be recycled by plants through photosynthesis, resulting in zero net emission of CO<sub>2</sub> thus consequently answering to the pollution problems tied to fuel production. In the present research work, highly activated Pd catalysts were prepared by employing mesoporous silica as the catalyst support for the hydrothermal deoxygenation of plant oil. Previous studies have found that Pd is an appropriate metal catalyst for the aqueous phase reforming (APR) reaction to produce the required hydrogen from glyceryl group of plant oil [4]. Moreover, the high surface area of mesoporous silica is useful in accommodating and dispersing the Pd metals, while its homogenous mesopores can bring about the fast internal mass transfer which increases the catalytic effectiveness factor [5]. Mesoporous silica is also mechanically and thermally stable which shows promising characteristics for our current application. For such reasons, the present work clearly enhances the originality of this research to achieve the sustainable production of drop-in fuel from plant oil.

## 2. Methods

The procedures for preparing mesoporous silica SBA-15 and MCM-41 are noted elsewhere [5, 6]. After the support synthesis, 4 wt.% Pd was impregnated onto the mesoporous silica through the incipient wetness impregnation (IWI) method with an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>4</sub>. The impregnated precursor was then calcined into the catalyst at 673 K under atmosphere for 2.0 h.

The catalytic reactions were performed in a 100-mL batch autoclave reactor. For the hydrothermal plant oil deoxygenation, 8 mL rapeseed oil and 4 mL distilled water were loaded with 0.50 g of the prepared catalyst into the vessel, which was consequently pressurized to 4 MPa with N<sub>2</sub> gas after purging air from the reaction space. The test reactions were conducted at 593 K for 1.5-6.0 hours, respectively. Meanwhile, for the isolated APR test reactions, 9 mL of 1-tetradecene and 3 mL of 10 wt.% glycerin solution were utilized. The chemical composition of the liquid products was then analyzed via gas chromatography (GC). From the GC data, the yield of products was determined based on their area percentage.

## 3. Results and discussion

The synthesized materials exhibited type IV N<sub>2</sub> isotherms with H1 hysteresis loops indicative of their mesoporous structures. After the impregnation of the Pd salt, the surface area was found to vary slightly as shown in Table 1. This implies that the metal salt may be residing on the surface of the support rather than on the pores as also shown by the minute change in the values of the pore volumes. Additionally, Pt supported on MCM-41 was prepared as reference catalyst for this study.

**Table 1.** Textural properties of the supports and their corresponding fresh catalysts.

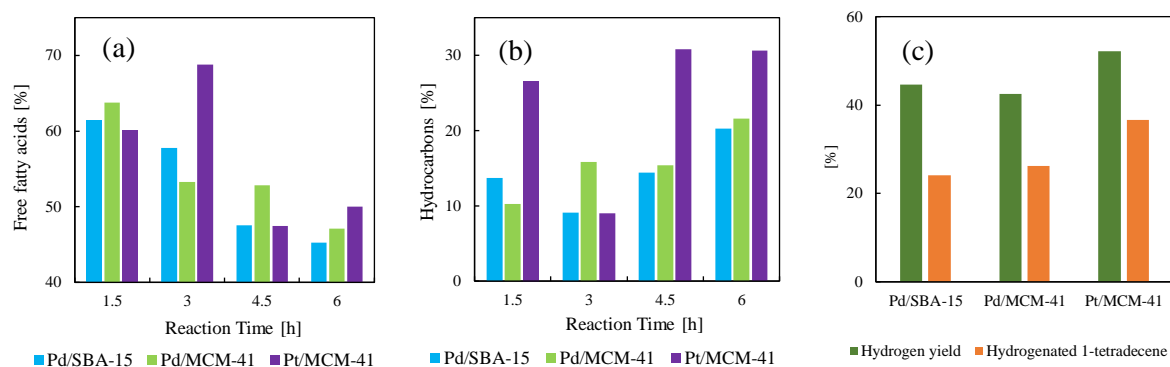
Material	Surface Area <sup>a</sup> [m <sup>2</sup> ·g <sup>-1</sup> ]	Pore Volume [cm <sup>3</sup> ·g <sup>-1</sup> ]	Mean Pore Diameter <sup>b</sup> [nm]
SBA-15	660.0	0.8	5.0
MCM-41	795.4	0.8	3.9
Pd/SBA-15	569.2	0.7	5.2
Pd/MCM-41	798.0	0.7	3.5

a Calculated by BET method

b Mean diameter calculated from pore volume and surface area

hydrogen between the prepared Pd catalysts after facilitating the APR reaction for 3.0 h at 593 K. Also, under the same APR conditions, the Pt catalyst resulted in the higher hydrogen yield than the Pd catalysts. While all the catalysts exhibit potential for producing the H<sub>2</sub> required for the deoxygenation of the plant oil into saturated hydrocarbons and utilizing the formed H<sub>2</sub> for the hydrogenation of the olefinic bonds during APR, less ideal products are formed during the deoxygenation reaction compared to that of the hydrogenated products in the isolated APR reaction. Two possibilities might have occurred during the deoxygenation reaction: (1) glycerol was not solely reformed into H<sub>2</sub> leading to the reduced available H<sub>2</sub> for complete deoxygenation of plant oil and (2) some of the produced H<sub>2</sub> from the *in-situ* APR were consumed in unwanted secondary reactions leading to reduced production in the desired hydrocarbons.

Figure 1a and 1b show that the Pd catalysts have similar FFA and HC yields at the end of 6.0 h, while the Pt/MCM-41 catalyst shows a higher HC yield of around 30% after reacting for the same time. It can be inferred that Pt metal has better hydrocarbon-forming capability under the current reacting conditions. Similar findings were observed for the APR reaction in Fig. 1c. There is no appreciable difference in the yields of



**Figure 1.** Differences in yields of products [free fatty acids (FFA), hydrocarbons (HC), hydrogen, hydrogenated 1-tetradecene] between Pd/SBA-15, Pd/MCM-41 and Pt/MCM-41 for the hydrothermal deoxygenation reaction (a)-(b) and isolated glycerol APR reaction (c) operated at 593 K.

#### 4. Conclusions

The mesoporous silica-supported catalysts were able to facilitate the H<sub>2</sub>-free catalytic hydrothermal deoxygenation of rapeseed oil at 593 K. The catalysts have shown positive time dependency for the formation of hydrocarbons reaching up to about 20% hydrocarbon formation for the Pd catalysts and around 30% for the Pt catalyst at 6.0 h. It was found that using Pt as the active metal loaded onto the support yielded to superior performance both in the hydrothermal deoxygenation of plant oil and the isolated APR. While SBA-15 was hypothesized to have better performance as a support for the active metal due to its bigger pores that can facilitate the diffusion of the reactants and products, MCM-41 performed just similarly as the former.

#### References

- [1] H. Kargbo, J. S. Harris, A. N. Phan, *J. Renew. Sustain. Energy*, 135 (2021) 110168
- [2] J. L. Holechek, H. M. Geli, M. N. Sawallah, R. Valdez, *Sustainability*, 14(8) (2022) 4792
- [3] R. Schäppi, D. Rutz, F. Dähler, A. Muroyama, P. Haueter, J. Lilliestam, A. Patt, P. Furler, A. Steinfeld, *Nature*, 601(7891) (2021) 63–68
- [4] R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic, *Appl. Catal. B: Environ.*, 43(1) (2003) 13–26
- [5] M. Kouzu, M. Kojima, K. Mori, S. Yamanaka, *Fuel Process. Technol.*, 217 (2021) 106831
- [6] H. Chen, Y. Wang, *Ceram. Int.*, 28(5) (2002) 541–547

#### Keywords

hydrothermal plant oil deoxygenation; drop-in fuel; renewable hydrogen; *in-situ* APR