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Mechanistic studies of lower temperature isomerization of n-heptane over fibrous silica molybdenum catalyst --Manuscript Draft--

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Abstract:	Platinum (Pt) inclusion on fibrous silica molybdenum (FSMO) and MoO ₃ /KCC-1 catalysts has been prepared and utilized for the lower temperature (200-350 °C) catalytic isomerization of n-heptane. The impact of Pt inclusion towards the structure, morphology, and acid distribution of catalysts was characterized by XRD, FTIR, N ₂ -physisorption, Py-IR, and H ₂ -IR. Compared with MoO ₃ /KCC-1, FSMO demonstrated superior MoO ₃ dispersion and amount of Lewis acid site associated with the in-situ synthesis technique. Although Pt inclusion slightly lessened acid sites due to inevitable partial coverage by the Pt cluster, the considerably higher amount of Lewis acid sites compared to Brønsted and conjugated sufficiently for generating protonic acid sites for enriching the isomerization activity. In contrast to Pt/MoO ₃ /KCC-1 and undoped catalysts, Pt/FSMO achieved a superior conversion of 70.9% with 63.6% isomer yield at a low temperature of 250 °C. The 28-h stability tests demonstrated that Pt/FSMO recorded stable isomerization activity, with a superior isomer yield (~48-52%) and inferior cracking yield (<3.0%) than Pt/MoO ₃ /KCC-1.

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05 MARCH 2023

Editor in Chief,
International Journal of Hydrogen Energy

Dear Prof,

Manuscript ID: HE-D-22-08512

Thank you very much for reviewing our manuscript and allowing us to revise the manuscript entitled “**Mechanistic studies of lower temperature isomerization of n-heptane over fibrous silica molybdenum catalyst**”. We are also grateful to the reviewers for the helpful comments. The manuscript has been revised after carefully considering the comments.

As described in the following pages, all the comments are addressed clearly and appropriately. In addition, some corrections have been made. All the changes are highlighted in yellow, as provided in the revised manuscript. We believe the revised manuscript is now acceptable for publication in the *International Journal of Hydrogen Energy*.

Thank you again for your time and consideration of this manuscript.

Sincerely yours,

Aishah Abdul Jalil (Ph.D)

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RESPONSE TO REVIEWERS

Manuscript Reference Number: HE-D-22-08512

Title: Mechanistic studies of lower temperature isomerization of n-heptane over fibrous silica molybdenum catalyst

The authors would like to appreciate the valuable comments from reviewers for improving our manuscript.

Reviewer #1

Comment 1:

What is the meaning of the word "Mechanistic" (in title of the article) in relation to this study?

Author reply:

In the context of our study, the term "mechanistic" refers to the investigation and understanding of the specific chemical reactions and steps that occur during the lower-temperature isomerization of n-C₇ over the FSMO. This involves identifying the intermediate species, reaction pathways, and the role of the catalyst in promoting the desired reaction. Essentially, our work proposed the underlying mechanisms that govern the n-C₇ isomerization process over FSMO, which is essential for optimizing the catalyst performance and designing more efficient and selective catalysts.

Comment 2:

In the experimental part, it's not quite clear at what stage of the synthesis molybdenum is added to the FSMO sample.

Author reply:

Thank you for the comment. The authors would like to apologize for the missing information. The authors already added the missing information in the experimental part, as highlighted in the revised manuscript.

"Thereafter, butanol and toluene were poured into the mixture under continuous agitation at ambient temperature before being dopped with the specified amount of MoO₃ seed." -Lines 113-115

Comment 3:

In the same part, the amount of molybdenum and platinum introduced into the catalysts should be indicated.

Author reply:

Thank you for the comment. In this work, the authors utilized molybdenum and platinum precursor to attain 10.0 wt% MoO₃ and 0.1 wt% Pt, respectively, during the synthesis Pt/FSMO and MoO₃/KCC-1 catalysts. As highlighted in the revised manuscript, the amount of molybdenum and platinum introduced into the catalysts has been added in the experimental part.

"For KCC-1 supported 10.0 wt% MoO₃ catalyst," -Line 124

"as the metal precursor (0.1 wt% Pt) over FSMO support" -Line 130

Comment 4:

Lines 214-215 the meaning of the sentence needs to be clarified - it seems that the meaning should be reversed. Since it is not the relative pressure of N₂ uptakes increased, but an increase in N₂ uptake at higher relative pressures.

Author reply:

Thank you for the comment. As advised, the authors have already rewritten the sentences as highlighted in the revised manuscript.

"However, when Pt was loaded onto the catalyst surface, the N₂ uptakes for Pt/MoO₃/KCC-1 increased substantially at higher relative pressure, while Pt/FSMO catalyst demonstrated an insignificant change." -Lines 216-218

Comment 5:

How was the average pore size calculated, which is presented in table 1? (it is desirable to clarify the formulas).

Author reply:

The authors want to sincerely apologize since we could not prove the calculation for the average pore size. The average pore size in Table 1 was measured by using BJH (Barrett-Joyner-Halenda) approach, automatically generated by the Beckman Coulter SA3100 unit. Based on the literature, the pore size distribution data were initially obtained using the BJH method. Then, the average pore diameter can be calculated by integrating the pore size distribution over the entire range of pore sizes and dividing it by the total pore volume. The equation for calculating the average pore diameter using the BJH method is:

$$\text{Average pore diameter} = \int D \cdot \text{PSD}(D) dD / \int \text{PSD}(D) dD$$

where D is the pore diameter and PSD is the pore size distribution.

Comment 6:

Fig 3b: y-axis for pore size distribution curves usually show dV/dr or dV/dD. Please explain why it is marked as dV/dp, what does "dp" mean? Also in the numerator is the change in pore volume, so the dimension should not be negative for "cm³" (cm³nm⁻¹g⁻¹).

Author reply:

Thank you for the comment. The authors want to apologize for our careless mistake. The authors agreed that in Fig 3b, the y-axis for pore size distribution curves should be "dV/dD", while the unit in "cm³ nm⁻¹ g⁻¹". Thus, the authors replaced the figure with the correct version, as provided in the List of Figures.

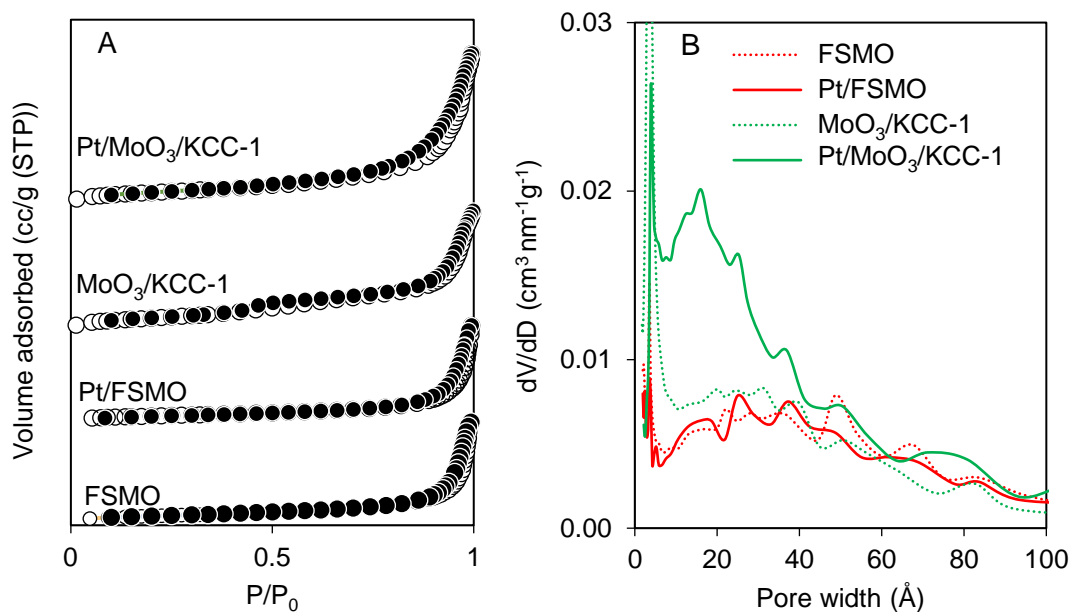


Fig. 3 N₂ adsorption-desorption and pore distribution for MoO₃-based catalysts

Comment 7:

According to IR studies (Figures 5-6): were extinction coefficients taken into account when calculating the number of BAS and LAS?

Author reply:

No. The authors only determine the qualitative presence or absence of basic and acidic sites on the surface of a material based on the intensity of the corresponding peaks.

Comment 8:

The reaction conditions (temperature, pressure, catalysts loading, molar ratio of hydrogen to n-heptane, raw material feed rate) should be indicated when studying the stability of catalysts (Fig. 8).

Author reply:

Thank you for the comment. As advised, the authors provided the reaction condition for the stability test in the caption for Fig. 8, as highlighted in the revised List of Figures.

Fig. 8 Catalyst stability test under 28 h time-on-stream at 250 °C, atmospheric pressure, and 0.2 g of catalyst. (2 μmol of n-C₇ + 100 ml min⁻¹ H₂)

Comment 9:

What explains the lower conversion of heptane at temperatures of 200 and 350°C for the sample with platinum (Pt/FSMO), compared to the sample without platinum (FSMO, Fig. 7)?

Author reply:

According to Ibrahim et al. (2020), the moderate Brønsted acid sites and abundant Lewis acid sites favours hydroisomerization, explaining the enhancement in the catalytic performance of Pt/HM@KCC-1. Regarding to this work, as seen in Fig. 7, although Pt/FSMO possessing abundant Lewis acid sites compared to FSMO, the inferior amount of Brønsted acid sites could explaining the lower conversion of heptane at temperatures of 200 °C. Similar phenomenon also occur at 350°C, which inferior amount of Brønsted and Lewis acid sites recorded for Pt/FSMO over FSMO.

References:

Ibrahim, M., Jalil, A. A., Khusnun, N. F., Fatah, N. A. A., Hamid, M. Y. S., Gambo, Y., Abdurashed, A. A., Hassan, N. S. (2020). Enhanced n-hexane hydroisomerization over bicontinuous lamellar silica mordenite supported platinum (Pt/HM@ KCC-1) catalyst. International Journal of Hydrogen Energy, 45(36), 18587-18599.

Comment 10:

It would be interesting to determine the coke content on the surface after 28 hours of testing Pt-FSMO and Pt/MoO₃/KCC-1 samples (Fig. 8).

Author reply:

Thank you for the comment. As requested, the authors have already added the temperature-programmed oxidation analysis to determine the coke content on the surface after 28 hours of testing Pt-FSMO and Pt/MoO₃/KCC-1 samples, as highlighted in the revised manuscript.

Temperature-programmed oxidation (TPO) was carried out in Mettler Toledo TGA/SDTA/851e Thermo-gravimetric unit to estimate the carbonaceous deposition on the surface of spent catalysts within the temperature of 10-900 °C. Lines-154-156

The temperature-programmed oxidation analysis was conducted to quantify the extent of carbonaceous deposition on the spent catalysts. As depicted in Fig. S1, it was evidenced that Pt/FSMO possessed an inferior amount of coke compared to Pt/MoO₃/KCC-1, further proving the stability of isomerization activity within 28 h reaction. Lines 347-350

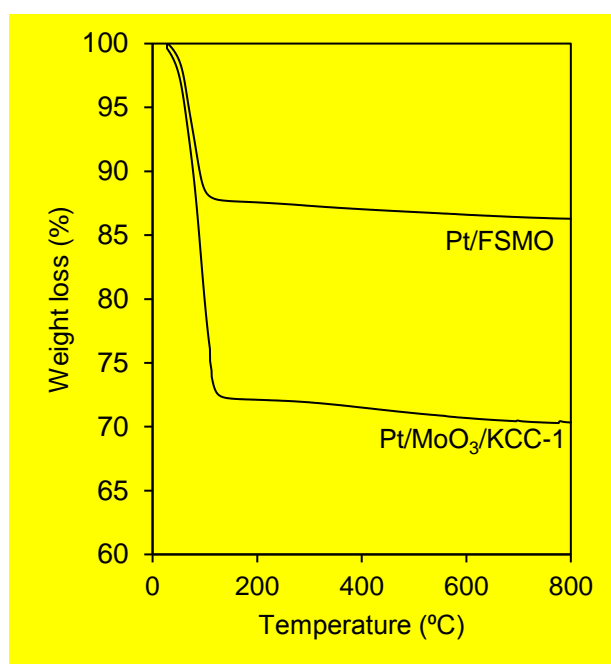


Fig. S1 TPO profile of spent Pt/FSMO and Pt/MoO₃/KCC-1 after catalyst stability test under

28 h time-on-stream at 250 °C

Comment 11:

Throughout the text of the article, there are two ways of writing of the fibrous silica molybdenum catalyst sample - FSMO and FSMo. In addition, there is a typo in line 352 - FSMO₃.

Author reply:

Thank you for the comment. The authors want to apologize for our mistake. The authors already rewrite the term used for fibrous silica molybdenum catalyst "FSMO" in the whole manuscript, as highlighted in the revised manuscript.

"fibrous structure of support with silica (FSMO)," – Line 353

Comment 12:

Line 427 - "isomerisation", in the rest of the text - "isomerization".

Author reply:

We want to apologize for our mistake. The authors already replaced "isomerisation" with "isomerization", as highlighted in the revised manuscript.

"Thus, isomerization activity improved, especially at the lower reaction temperature." -Line 428

Comment 13:

Lines 447 and 448 - need to make a subscript for the formula "MoO3".

Author reply:

We want to apologize for our mistake. The authors already make a subscript for the formula "MoO₃", as highlighted in the revised manuscript.

"compared to MoO₃/KCC-1, regardless of" -Lines 448-449

Comment 14:

For the entire list of references, it is necessary to check the subscripts in chemical formulas. Also note that there is not enough data for reference [37] (volume number, page number).

Author reply:

We want to apologize for our mistake. The authors already checked all the subscripts issues in references and provided the volume number, page number for reference [37], as highlighted in the revised manuscript.

[37] Azami MS, Jalil AA, Aziz FFA, Hassan NS, Mamat CR, Izzudin NM. Influence of the nitrogen pots from graphitic carbon nitride with the presence of wrinkled silica-titania for photodegradation enhancement of 2-chlorophenol. International Journal of Hydrogen Energy. 2021;48:6532-6545.

[38] Aziz FFA, Jalil AA, Triwahyono S, Mohamed M. Controllable structure of fibrous SiO₂-ZSM-5 support decorated with TiO₂ catalysts for enhanced photodegradation of paracetamol. Applied Surface Science. 2018;455:84-95.

Comment 15:

Line 162 - written "n-C5" instead "n-C7".

Author reply:

We want to apologize for our careless mistake. The authors already replaced "n-C₅" with "n-C₇", as highlighted in the revised manuscript.

"about two μmol of n-C₇ was driven into" - Line 165

Comment 16:

Line 165 - temperature is given in kelvins (77 K), while the rest of the text uses degrees Celsius.

Author reply:

Thank you for the comment. The authors already replaced temperature unit "77" with "-196 °C", as highlighted in the revised manuscript.

"The isomerization product was confined using N₂ (-196 °C)" - Line 165

Comment 17:

Line 297 - please clarify "-H" is a hydride ion designation?

Author reply:

Thank you for the comment. We want to apologize for our mistake. That "-H" corresponds to the hydrogen atom from the Si-OH bond. The incorporation of MoO₃ in the fibrous silica framework resulted in more hydrogen atom replacement by Mo ions to form Si-O-Mo, associated with the alternately aligned SiO₂ and MoO₃ in the fibrous structure compared to MoO₃/KCC-1. In order to avoid confusion, the author already replaced "-H" with "hydrogen atom", as highlighted in the revised manuscript.

"there was more replacement of hydrogen atom (from Brønsted Si-OH) by Mo ions in forming Si-O-Mo (Lewis acid sites)." - Line 298

Comment 18:

It is need to specify decryption for Y_{hhc} (figs. 7, 8).

Author reply:

Thank you for the comment. As advised, the authors added the description for Y_{hhc} in the figure caption, as highlighted in the revised List of Figures.

“**Fig. 7** *n*-heptane isomerization activity over MoO₃-based catalyst at elevated temperature (Y_{iso}= yield of isomer, Y_{cracking} = Yield of cracking, and Y_{hhc} = Yield of higher hydrocarbon)”

Reviewer #2

Comment 1:

Line 159: Why is oxygen stream used? What is the need for this work?

Author reply:

Thank you for the comment. The purpose of treating the tested catalyst with oxygen is to remove any impurities or residues that may be present on the surface of the catalyst. These impurities can interfere with the activity and selectivity of the catalyst during the reaction.

Comment 2:

Line 162: Why was normal pentane (n-C₅) injected into the reactor? Unless the isomerization of normal heptane is not the goal of the work?

Author reply:

The authors would like to apologize for our careless mistake. The authors already replaced "n-C₅" with "n-C₇", as highlighted in the revised manuscript.

"about two μmol of n-C₇ was driven into" - Line 165

Comment 3:

Line 165: What is the need to use nitrogen carrier gas to transfer products to GC? In this way, it seems that at the used temperature, the products are completely gaseous, and if GC Online is used, the products are injected into it online.

Author reply:

Thank you for the comment. In this work, the authors did not use nitrogen as a carrier to transfer the products to GC. The outlet stream was immersed in liquid nitrogen before flash-evaporating into the gas chromatograph system. This approach was applied because of:

- i) The low temperature of liquid nitrogen helps to quench the isomerization reaction, stopping any further changes to the product. This part is important because

isomerization reactions can be temperature-sensitive and may continue to occur even at lower temperatures.

- ii) The cold temperature of liquid nitrogen also helps to condense and remove any volatile impurities or byproducts that may have formed during the reaction. This condition helps to ensure that only the desired product is analyzed in the gas chromatograph system, improving the accuracy and precision of the analysis.

Finally, the flash-evaporation of the isomerization product from the liquid nitrogen into the gas chromatograph system ensures that the sample is quickly vaporized and carried by the carrier gas through the column for separation and detection. This step is crucial because it helps to minimize any potential losses or degradation of the sample during the sample introduction process.

Comment 4:

It is necessary to state the information of GC used.

Author reply:

Thank you for the comments. The information on GC used in this isomerization work has already been mentioned in the experimental part. The authors used an online 6090 N Agilent gas chromatograph equipped with HP-5 Capillary Column and FID detector to analyse the isomerization product.

"An online gas chromatograph (Agilent 6090N, FID, HP-5), connected with a utilized micro-catalytic pulse reactor, scrutinized the isomerization product." Lines 164-165

Comment 5:

Line 169: The definition of selectivity used does not seem to be correct. Refer to the references and use a better definition for selectivity.

Author reply:

Thank you for the comment. The authors would like to apologize for our mistake. The formula with the definition used to estimate the isomerization activity was rewritten, as highlighted in the revised manuscript.

$$X_i(\%) = \frac{\sum A_i - A_{r,i}}{\sum A_i} \times 100\% \quad (1)$$

$$S_i(\%) = \frac{A_i}{\sum A_i - A_{r,i}} \times 100\% \quad (2)$$

$$Y_i = \frac{X_i \times S_i}{100} \quad (3)$$

Where A_i = corrected chromatographic area for a specific product and $A_{r,i}$ = corrected chromatographic area for residual of n-heptane species, in weight percent unit.

References:

[1] Setiabudi, H. D., Jalil, A. A., Triwahyono, S., Kamarudin, N. H. N., & Mukti, R. R. (2012). IR study of iridium bonded to perturbed silanol groups of Pt-HZSM5 for n-pentane isomerization. *Applied Catalysis A: General*, 417, 190-199.

[2] Ruslan, N. N., Fadzlillah, N. A., Karim, A. H., Jalil, A. A., & Triwahyono, S. (2011). IR study of active sites for n-heptane isomerization over MoO₃-ZrO₂. *Applied Catalysis A: General*, 406(1-2), 102-112.

Comment 6:

What percentage of metals (platinum and molybdenum) have been used to prepare the catalysts? Why?

Author reply:

Thank you for the comment. In this work, the authors utilized molybdenum and platinum precursor to attain 10.0 wt%MoO₃ and 0.1 wt%Pt, respectively, during Pt/FSMO and MoO₃/KCC-1 catalysts preparation. As highlighted in the revised manuscript, the amount of molybdenum and platinum introduced into the catalysts has been added.

"For KCC-1 supported 10.0 wt%MoO₃ catalyst," -Line 124

"as the metal precursor (0.1 wt%Pt) over FSMO support" -Line 130

- 0.1 wt%Pt was applied since several studies claimed that adding 0.1% of Pt increases activity and stability during isomerization. However, the increase in Pt content resulted in a decrement in isomerization activity

References:

[1] Grau, J. M., Yori, J. C., & Parera, J. M. (2001). Hydroisomerization–cracking of n-octane on Pt/WO₄–ZrO₂ and Pt/SO₄–ZrO₂: Effect of Pt load on catalyst performance. *Applied Catalysis A: General*, 213(2), 247-257.

[2] Yang, L., Song, Z., Yu, Y., Zhu, L., & Xia, D. (2020). Bimetallic bifunctional Pt-NiP/H β as a novel and highly efficient catalyst for n-hexane isomerization. *Catalysis Surveys from Asia*, 24, 104-114.

[3] Zhang, A., Nakamura, I., Aimoto, K., & Fujimoto, K. (1995). Isomerization of n-pentane and other light hydrocarbons on hybrid catalyst. Effect of hydrogen spillover. *Industrial & engineering chemistry research*, 34(4), 1074-1080.

-10.0 wt%MoO₃ was applied since, in literature, this amount led to the highest Brønsted acid to metal-like sites ratio, resulting in the best hydroconversion of alkane.

References:

[1] Oloye, F. F., & Ololade, I. A. (2018). Influence of molybdenum loadings on the properties of MoO₃/zirconia catalysts. *Chemistry Africa*, 1(3-4), 119-126.

[2] Triwahyono, S., Jalil, A. A., Azman, H. A., & Mamat, C. R. (2015). Isomerization of C₅-C₇ Linear Alkanes over WO₃-ZrO₂ under Helium Atmosphere. *Jurnal Teknologi*, 75(6).

[3] Chen, J., Duan, Z., Song, Z., Zhu, L., Zhou, Y., Xiang, Y., & Xia, D. (2017). Relationship between surface property and catalytic application of amorphous NiP/H β catalyst for n-hexane isomerization. *Applied Surface Science*, 425, 448-460.

Comment 7:

It is better to make the XRD shape clearer and bigger and show the Miller indices on the peaks.

Author reply:

Thank you for the comment. As requested, the XRD patterns in Fig. 1 have been redrawn and included with the Miller indices on the peaks.

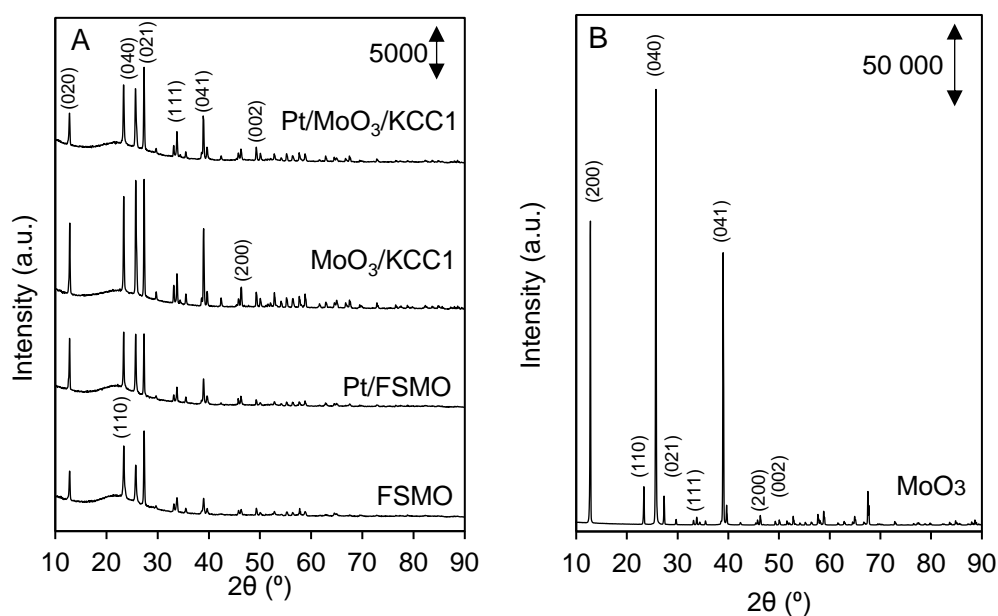


Fig. 1 XRD diffractogram for (A) MoO₃-based catalysts and (B) commercial MoO₃

Comment 8:

To express the stability of the catalysts against coke, the TGA spectra of these catalysts must be expressed.

Author reply:

Thank you for the comment. As requested, the authors have already added the temperature-programmed oxidation analysis to determine the coke content on the surface after 28 hours of testing Pt-FSMO and Pt/MoO₃/KCC-1 samples, as highlighted in the revised manuscript.

Temperature-programmed oxidation (TPO) was carried out in Mettler Toledo TGA/SDTA/851e Thermo-gravimetric unit to estimate the carbonaceous deposition on the surface of spent catalysts within the temperature of 10-900 °C. Lines-154-156

The temperature-programmed oxidation analysis was conducted to quantify the extent of carbonaceous deposition on the spent catalysts. As depicted in Fig. S1, it was evidenced that Pt/FSMO possessed an inferior amount of coke compared to Pt/MoO₃/KCC-1, further proving the stability of isomerization activity within 28 h reaction. Lines 347-350

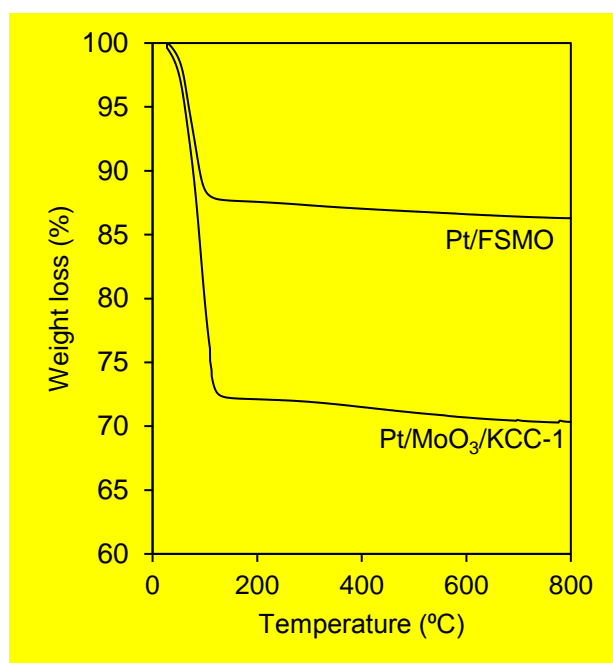
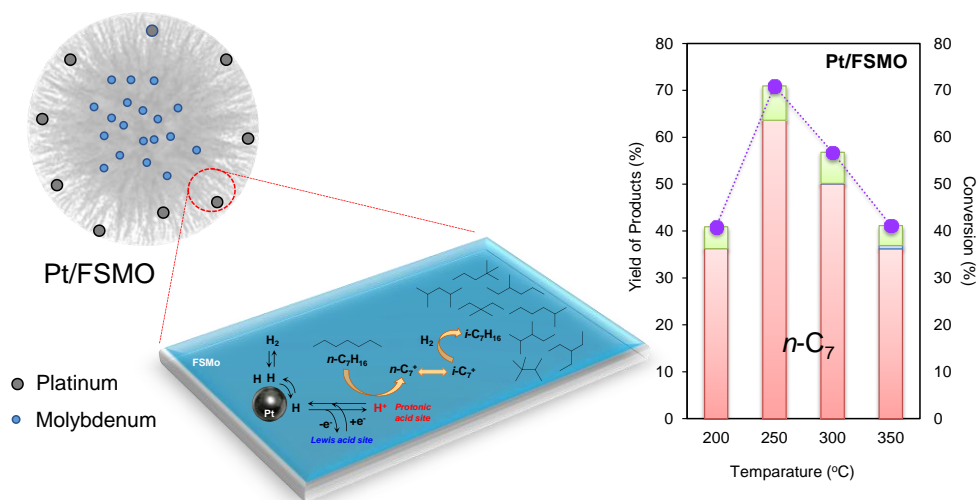


Fig. S1 TPO profile of spent Pt/FSMO and Pt/MoO₃/KCC-1 after catalyst stability test under 28 h time-on-stream at 250 °C

HIGHLIGHTS

- FSMO, MoO₃/KCC-1, Pt/FSMO, and Pt/MoO₃/KCC-1 was synthesized for C₇ isomerization
- Mo insertion in Si-matrix induced Si-O-Mo formation, intensifying Lewis acid sites
- Pt inclusion promoted H₂ dissociation and enriched the amount of Lewis acid sites
- The highest *i*-C₇ yield of about 63.6% was attained for Pt/FSMO at 250 °C
- Excellent stability with low cracking revealed by Pt/FSMO compared to Pt/MoO₃/KCC-1

GRAPHICAL ABSTRACT



1 **Mechanistic studies of lower temperature isomerization of n-heptane over fibrous silica**
2 **molybdenum catalyst**

3

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26

27 **Abstract**

28

29 Platinum (Pt) inclusion on fibrous silica molybdenum (FSMO) and MoO₃/KCC-1 catalysts has
30 been prepared and utilized for the lower temperature (200-350 °C) catalytic isomerization of n-
31 heptane. The impact of Pt inclusion towards the structure, morphology, and acid distribution
32 of catalysts was characterized by XRD, FTIR, N₂-physisorption, Py-IR, and H₂-IR. Compared
33 with MoO₃/KCC-1, FSMO demonstrated superior MoO₃ dispersion and amount of Lewis acid
34 site associated with the in-situ synthesis technique. Although Pt inclusion slightly lessened acid
35 sites due to inevitable partial coverage by the Pt cluster, the considerably higher amount of
36 Lewis acid sites compared to Brønsted and conjugated sufficiently for generating protonic acid
37 sites for enriching the isomerization activity. In contrast to Pt/MoO₃/KCC-1 and undoped
38 catalysts, Pt/FSMO achieved a superior conversion of 70.9% with 63.6% isomer yield at a low
39 temperature of 250 °C. The 28-h stability tests demonstrated that Pt/FSMO recorded stable
40 isomerization activity, with a superior isomer yield (~48-52%) and inferior cracking yield
41 (<3.0%) than Pt/MoO₃/KCC-1.

42

43 *Keywords:* n-C₇ isomerization; MoO₃-based catalysts; Platinum; Lewis acid; Protonic acid
44 side

45 1.0 Introduction

46

47 Globally, comprehensive research and development initiatives have been undertaken to
48 produce clean gasoline with low aromatics, olefins, sulphur, and high-octane numbers, in
49 response to growing concerns over energy and environmental issues [1]. As a result, *n*-alkane
50 isomerization has gained popularity as a safe and environmentally friendly method for
51 enhancing gasoline quality [2]. This pathway allows *n*-alkanes with a linear carbon chain to be
52 converted into branched isomers with a high research octane number (RON) [3, 4]. So far,
53 tremendous effort has been put forth in researching light alkane isomerization since this
54 compound processing has been industrialised. Yet, this technique has not been utilized for *n*-
55 heptane and heavier alkanes due to the higher tendency of excessive development of cracking
56 products as the conversion rate increases, leading to the deactivation of the catalyst due to the
57 accumulation of coke on the surface's catalysts [5]. Hence, considering potential
58 implementation, it is critical to look for relatively efficient and selective catalysts for heavy *n*-
59 heptane isomerization while concurrently limiting cracking activities.

60 Bifunctional heterogeneous catalyst materials consisting of acidic supporting materials
61 as well as hydrogenation/hydrogenation metal sites are among the popular catalysts used for
62 the catalytic acid reaction [6, 7]. Both metallic and acidic functions influence the catalyst's
63 properties and facilitate the alkane hydro-conversion. For instance, metal sites could generate
64 carbonium ions via alkane dehydrogenation, a crucial intermediate species for initiating
65 isomerization and cracking [8]. Once the acidity of the catalyst is mild, and the
66 dehydrogenation activity of metal is substantial, a high yield of isomers is generated. In
67 addition, when the dehydrogenation activity is more significant, unsaturated products are more
68 hydrogenated, thus, inhibiting the escape acid-catalyzed skeleton rearrangement and cracking
69 [9]. Throughout the scientific literature, *n*-alkane isomerization has made considerable use of

70 catalysts such as noble metals supported on microporous and mesoporous materials. In fact, it
71 was found that the hydrogen atom spillover mechanism used by bifunctional heterogeneous
72 catalysts could strongly induce isomerization [10]. Numerous acid-catalyzed reactions using
73 various types of catalysts, like Pt/MoO₃ [11-13], Pt/WO₃-ZrO₂ [14], MoO₃/MSN [15], and
74 Zn/HZSM-5 [10], have been explored for their spillover mechanisms.

75 Recently, the potential of the MoO₃ type catalysts has been extensively explored for a
76 wide range of catalytic processes like methanation, olefin metathesis, alcohols oxidation, and
77 isomerization accredited to MoO₃'s exceptional features, including excellent stability and
78 regeneration performance [16]. In addition, MoO₃ possessed both Lewis and Bronsted acid
79 sites, which is crucial for *n*-alkane isomerization and provides superior selectivity for heptane
80 isomerization compared to conventional catalysts. Incorporating second material as active sites
81 into bifunctional catalysts has aroused considerable attention in recent years owing to the
82 positive effects on isomerization performance, isomer selectivity, as well as stability. Second
83 Noble materials like Pd and Pt have been extensively studied, attributed to their hydrogen
84 spillover capability, boosting the isomerization activity. Indeed, the combination between Pt
85 and MoO₃ in a hydrogen atmosphere can generate several active species, including H_xMoO₃
86 and MoO₂, that are utilized for isomerization [11, 17]. Previous work has demonstrated that
87 incorporating Pt and MoO₃ into diverse supporting materials effectively improved *n*-heptane
88 isomerization performance [11, 13]. Regrettably, it should be noted that there is a paucity of
89 literature focusing on the usage of catalysts at low operating temperature.

90 Creating support with a dendrimer fibrous structure has recently received much
91 attention [18]. This strategy can produce an ideal support material possessing vast surface area,
92 tuneable pore volume, conveniently reachable inner surface, as well as superior thermal
93 stability [19-21]. In fact, this approach has resulted in a positive effect on the catalytic activity
94 of all catalytic pathways, including isomerization [4], methanation [22], cumene cracking [23],

95 and dry reforming [24]. According to the researchers, the improvement was attributable to the
96 enhanced accessibility of active areas within this particular shape. Inspired by the previous
97 study, we synthesized fibrous silica-molybdenum trioxide (FSMO) supported platinum (Pt)
98 and assessed their capability in *n*-heptane isomerization at low reaction temperature for the first
99 time. The fibrous silica in the Pt/FSMO catalyst induces Si-O-Mo formation to enhance Lewis
100 acid site quantity, which will cause a growth in protonic acid site generation, thus enriching *n*-
101 heptane isomerization activity. The physicochemical features of the studied catalysts were
102 analysed in detail via XRD, N₂ physisorption and several in-situ IR analysis. The isomerization
103 pathway over Pt/FSMO catalyst is also elucidated.

104

105

106 **2.0 Experimental**

107

108 *2.1 MoO₃-based catalysts synthesis*

109

110 Fibrous silica-molybdenum (FSMO) and KCC-1 were prepared corresponding to the
111 microemulsion approach as detailed in the literature [25, 26]. In brief, a homogeneous solution
112 consisting of CTAB and urea was acquired by mixing and stirring both chemicals in distilled
113 water for 15 min (25°C). Thereafter, butanol and toluene were poured into the mixture under
114 continuous agitation at ambient temperature before being dopped with the specified amount of
115 MoO₃ seed. The resulting mixture was further agitated at ambient temperature for two hours to
116 guarantee TEOS was hydrolyzed entirely prior to the six-hour hydrothermal treatment in
117 microwave irradiation (120 °C, 400 W). Afterwards, the acquired solution was air-dried in an
118 oven (24 h, 110 °C) to eradicate the moisture before furnace-calcination (6 h, 550 °C) to gain
119 desired FSMO. On the contrary, for KCC-1 support production, TEOS was dropped along with

120 butanol and toluene before being treated with a similar condition for hydrothermal treatment,
121 air-drying, and furnace-calcination.

122 The incipient wetness impregnation technique, as reported by Siang et al. [27], was
123 applied in this work to generate Pt/FSMO and MoO₃/KCC-1 catalysts. For KCC-1 supported
124 10.0 wt% MoO₃ catalyst, a calculated amount of ammonium heptamolybdate ([NH₄]₆Mo₇O₂₄)
125 as the metal precursor and KCC-1 support were separately dissolved in the deionized water
126 prior to the impregnation step. After both solutions were mixed and agitated at ambient
127 temperature for four hours, the resulting mixture was further air-dried in an oven (24 h, 110
128 °C) and subsequently underwent furnace-calcination (6 h, 550 °C), which yielded MoO₃/KCC-
129 1. A similar approach as those stated earlier was employed to prepare Pt/FSMO using
130 chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) as the metal precursor (0.1 wt% Pt) over
131 FSMO support. For Pt/MoO₃/KCC-1 catalyst preparation, the sequential incipient wetness
132 impregnation technique was employed by discretely dissolved H₂PtCl₆·6H₂O and as-
133 synthesized MoO₃/KCC-1 in deionized water. Afterwards, both dissolved materials were
134 combined, agitated, dried, and calcined, similar to those earlier impregnation steps to acquire
135 Pt/MoO₃/KCC-1.

136

137 2.3 Characterizations of MoO₃-based catalysts

138

139 The crystalline structure of studied catalysts was assessed by X-ray diffractogram ($2\theta =$
140 $20-85^\circ$, step size = 0.02) on a Bruker Advance D8 diffractometer equipped with Cu Ka
141 radiation ($\lambda = 0.154$ nm, V = 40 kV, I = 40m A). The Barrett-Joyner-Halenda (BJH) and
142 Brunauer-Emmet-Teller (BET) techniques were applied to measure the catalyst's surface area
143 and pore properties using liquid nitrogen at -196 °C in a Beckman Coulter SA3100 unit. The
144 one-hour-outgassed treatment was initially employed at 300 °C prior to the nitrogen adsorption

145 at 77 K for eradicating the moisture and contaminants. The functional groups of the studied
146 catalysts were appraised via the FTIR-KBr approach at the range of 1600-400 cm^{-1} with 5 cm^{-1}
147 resolutions on the FT-IR spectrometer unit (Agilent Cary 660). The acidity of studied catalysts
148 was scrutinized through Py-IR adsorption on stainless-steel cells with two CaF_2 windows
149 sealed. Initially, the tested catalysts were pelletized before exposing them to 4 Torr of pyridine
150 stream for a quarter-hour at 150 °C. Afterwards, the desorption of pyridine from tested catalysts
151 was carried out at a different temperature within 150-350°C. H_2 -IR adsorption was also
152 operated in similar equipment for Py-IR adsorption. After activation treatment, the tested
153 catalysts were cooled to room temperature before being subjected to 20 Torr of the hydrogen
154 stream under rising temperature up to 350 °C. Temperature-programmed oxidation (TPO) was
155 carried out in Mettler Toledo TGA/SDTA/851e Thermo-gravimetric unit to estimate the
156 carbonaceous deposition on the surface of spent catalysts within the temperature of 10-900 °C.

157

158 2.4 *n-C₇ Isomerization evaluation*

159

160 The micro-catalytic pulse reactor was utilized to evaluate *n*-heptane isomerization within
161 200-350 °C. About 0.2 g of the studied catalyst was employed in the reactor, followed by
162 exposure to the 100 ml min^{-1} of O_2 stream (1 h, 400 °C) and then 100 ml min^{-1} H_2 stream (3 h,
163 400 °C) as the pre-treatment step. Subsequently, the tested catalyst was cold down in a similar
164 H_2 stream to reach 150 °C. After stabilizing and reaching the necessary conditions, about two
165 μmol of *n-C₇* was driven into the reactor filled with an H_2 stream (100 ml min^{-1}) to commence
166 the isomerization process. An online gas chromatograph (Agilent 6090N, FID, HP-5),
167 connected with a utilized micro-catalytic pulse reactor, scrutinized the isomerization product.
168 The isomerization product was confined using N_2 (-196 °C) before being flash-evaporated into

169 the gas chromatograph system. The isomerization activity was estimated based on the
170 conversion (X), yield (Y), and selectivity (S), as expressed in Eqs. (1)-(3).

$$171 \quad X_i(\%) = \frac{\sum A_i - A_{r,i}}{\sum A_i} \times 100\% \quad (1)$$

$$172 \quad S_i(\%) = \frac{A_i}{\sum A_i - A_{r,i}} \times 100\% \quad (2)$$

$$173 \quad Y_i = \frac{X_i \times S_i}{100} \quad (3)$$

174 Where A_i = corrected chromatographic area for a specific product and $A_{r,i}$ = corrected
175 chromatographic area for residual of n-heptane species, in weight percent unit.

176

177

178 3.0 Results and Discussion

179

180 3.1 Characterization analysis

181

182 XRD diffractograms for commercial MoO₃ and generated catalysts are shown in Figs.
183 1A-B. All of the prepared catalysts showed a clear peak at $2\theta = 10^\circ$ - 70° on the plot. The
184 XRD pattern of the MoO₃ catalyst demonstrated that it possesses an orthorhombic structure
185 consistent with standard data (JCPDS Card No: 050508) [28]. The crystallite peaks
186 corresponded to the MoO₃ witnessed at an angle of 2θ about 12.9° (020), 23.4° (110), 25.8°
187 (040), 27.4° (021), 33.7° (111), 39.0° (041), 46.1° (200), and 49.4° (002) in FSMO and
188 MoO₃/KCC-1 [29]. The inferior intensity of crystallite peaks of FSMO than MoO₃/KCC-1
189 catalyst, indicating that the in-situ synthesis strategy for generating FSMO promoted the well-
190 distribution of Mo on the Si framework in comparison to MoO₃/KCC-1 prepared via the
191 incipient wetness impregnation approach [30]. Furthermore, due to the small size of the Pt

192 species dispersed on the FSMO and MoO₃/KCC-1, possibly below than XRD detection limit,
193 further explained for no visible diffraction peaks assignable to Pt species over Pt/FSMO and
194 Pt/ MoO₃/KCC-1 [31].

195 The FTIR spectra (1400-400 cm⁻¹) of the functional groups owned by studied catalysts
196 are depicted in Fig. 2. Evidently, all the studied catalysts displayed five identical IR bands
197 ranging from 1095 cm⁻¹ to 467 cm⁻¹. The absorption peaks appeared at a wavenumber of 1095
198 cm⁻¹, 956 cm⁻¹, 802 cm⁻¹, and 467 cm⁻¹ are linked to the vibration of asymmetric Si-O-Si,
199 external Si-OH, symmetric Si-O-Si, and bending Si-O-Si, respectively [32]. Meanwhile,
200 absorption peaks identified at a wavenumber of 902 cm⁻¹ overall studied catalysts signified
201 weak Mo=O vibration [33, 34]. Following the modification of MoO₃ into FSMO, a drop in the
202 intensity for the IR band at 956 cm⁻¹ (external Si-OH vibration) for FSMO compared to
203 MoO₃/KCC-1 suggesting that more replacement of hydrogen atom by Mo ions to form Si-O-
204 Mo, associated with the alternately aligned SiO₂ and MoO₃ in the fibrous structure. As a
205 consequence, this improvement could strengthen the interaction of MoO₃-SiO₂. This
206 observation was also reported by Sawal et al. [35] and Hitam et al. [36]. Remarkably, the FTIR
207 spectrum of FSMO was almost identical to that of Pt/FSMO, revealing no significant changes
208 towards the silicate framework of FSMO after Pt incorporation. Apart from that, it is apparent
209 from these FTIR spectra that most of the IR bands for FSMO and MoO₃/KCC-1 catalysts
210 experienced a slight decrease in intensity compared to Pt-loaded catalysts, indicating the
211 successful impregnation of Pt over the tested catalysts, creating new interaction between Pt and
212 SiO₂.

213 Further investigation was performed using N₂ physisorption analysis to examine
214 synthesized catalysts' textural properties; the results are presented in Fig. 3. As can be observed,
215 all the prepared catalysts demonstrated a type IV isotherm profile with a typical H3 hysteresis
216 loop, confirming the mesoporous structure characteristic of the synthesized catalysts (Fig. 3A)

217 [30]. In addition, in the absence of Pt element, both FSMO and MoO₃/KCC-1 catalysts
218 exhibited comparable N₂ uptakes. However, when Pt was loaded onto the catalyst surface, the
219 N₂ uptakes for Pt/MoO₃/KCC-1 increased substantially at higher relative pressure, while
220 Pt/FSMO catalyst demonstrated an insignificant change. This result may be explained by the
221 fact that high interaction between the Pt element and MoO₃ of Pt/MoO₃/KCC-1 reduced the
222 pore blockage of the MoO₃ on the mesopore of the KCC-1 [36]. Besides, the total pore volume
223 for MoO₃/KCC-1 catalyst increased after adding Pt (Table 1), which indirectly supported the
224 earlier statement. Meanwhile, for Pt/FSMO catalyst, the pore volume was slightly decreased
225 compared to the FSMO catalyst, suggesting the filling of Pt inside the FSMO mesopore [30].

226 Barrett-Joyner- Halenda (BJH) approach was applied to assess the average pore
227 diameter, as shown in Fig. 3B. The BJH pore size distribution demonstrated the pore diameter
228 of the synthesized catalysts placed within 3-40 (Å), showing the intrinsic of mesopores
229 features. It is worth noting that the pore distribution of FSMO and KCC-1-supported MoO₃
230 catalysts were considerably grown by adding Pt, probably due to the high mesoporous of Pt
231 that created inter-dendrimer distances [37]. For a better understanding of the textural properties
232 of as-prepared catalysts, the results were tabulated and presented in Table 1. As noticed, the
233 surface area for both FSMO (114.6 m²/g) and MoO₃/KCC-1 (221.3 m²/g) was reduced
234 considerably after adding Pt, suggesting that pores of FSMO and MoO₃/KCC-1 catalysts were
235 partially blocked by Pt particles [38]. This trend further inferred that the alteration of catalyst
236 structure could lead to surface area changes.

237 The efficacy of the isomerization reaction was considerably linked to the number and
238 intensity of the surface acidity in catalysts. Thus, Py-IR measurement was applied to assess the
239 distribution of Lewis and Brønsted acidic sites over activated catalysts at different temperatures
240 (150-250 °C), and the Py-IR spectra are illustrated in Fig. 4. As can be seen, all of the studied
241 catalysts disclosed three IR bands ranging within 1570-1420 cm⁻¹. It was noted that IR bands

242 spotted at 1454 cm^{-1} and 1539 cm^{-1} belonged to pyridinium ions adsorption on Lewis and
243 Brønsted acid sites, respectively [39, 40]. In addition, the appearance of IR band at a
244 wavenumber of 1488 cm^{-1} over all tested catalysts related to Brønsted and Lewis acid sites
245 combination [41, 42]. Interestingly, by comparing FSMO and $\text{MoO}_3/\text{KCC-1}$, it was noticed
246 that Lewis acid sites intensity for FSMO was considerably higher than KCC-1 supported MoO_3
247 catalysts, possibly ascribed to the more replacement of -H (from Brønsted) by Mo ions in
248 forming Si-O-Mo (Lewis acid sites), resulted from the fibrous framework, in line with FTIR
249 finding. The decline in Lewis and Brønsted acid site intensity was witnessed after Pt was
250 impregnated onto FSMO and $\text{MoO}_3/\text{KCC-1}$, suggesting the inevitable partial coverage of
251 acidic sites by the Pt cluster. A comparable phenomenon was claimed by Setiabudi et al. [43]
252 and Teh et al. [5] during the isomerization over Ir/Pt-HZSM5 and Pt/ MoO_3 -HBEA catalysts,
253 respectively.

254 The impact of outgassed temperature ($150\text{-}350\text{ }^\circ\text{C}$) towards the distribution of acidic
255 sites on studied catalysts is also elucidated in Fig. 4. The pyridine molecules adsorbed on weak
256 acid sites typically desorbed at a lower temperature whilst higher outgassing temperature is
257 required for desorbing pyridine molecules for strong acid sites. All tested catalysts appeared to
258 demonstrate intense interaction between pyridine and acidic sites at $150\text{ }^\circ\text{C}$ and remained firm
259 at the outgassing temperature of $150\text{ }^\circ\text{C}$. The considerable decline in the intensity of acidic sites
260 for all studied catalysts was evidenced along with the rising outgassing temperature of up to
261 $350\text{ }^\circ\text{C}$, signifying that weak-to-moderate Brønsted and Lewis acid sites are dominantly located
262 on those catalysts. This outcome also accords with the trends observed by other studies by
263 Fatah et al. [15] and Ma et al. [44] during the Py-IR evaluation over Pt/MSN, MoO_3/MSN , and
264 Al/SBA catalysts, respectively. Previous studies on isomerization have noted that the more
265 significant amount and intensity of acid sites of catalysts favour cracking instead of

266 isomerization reaction [5, 45]. Thus, the optimum amount with moderate acid sites is preferable
267 for enhanced isomerization.

268 Fig.5 disclosed the Py-IR spectra in 1600-1400 cm^{-1} when the pyridine pre-adsorbed
269 catalysts were heated in H_2 gas at elevated temperatures. The heating of all catalysts under H_2
270 gas exposure modified the intensity of Lewis and Bronsted acid sites at 1446 cm^{-1} and 1538
271 cm^{-1} , respectively. Particularly, the intensity of Lewis acid sites declined with the simultaneous
272 rise in the Bronsted acid sites, indicating the formation of protonic acid sites from hydrogen
273 atoms spillover [4]. In general, protonic acid sites formed through interconversion of the Lewis
274 acid sites. In this study, the protonic acid site formation rate is higher in all catalysts at lower
275 temperatures (250-300 $^\circ\text{C}$), as presented in Fig. 6. For FSMO and $\text{MoO}_3/\text{KCC-1}$, the formation
276 of protonic acid sites was probably due to the interaction of the Mo atom with the proton in the
277 form $(\text{MoO}_x)\text{-(H}_y\text{)}^+$ that generated from releasing of the electron by atomic hydrogen, as
278 similarly reported by previous studies [15]. Interestingly, adding Pt into both catalysts
279 significantly increased the protonic acid site formation rate, especially at low operating
280 temperatures. These results indicated that Pt heightened the interaction of the hydrogen atom
281 with the surface of FSMO and $\text{MoO}_3/\text{KCC-1}$. This phenomenon has also been observed in
282 Pt/ $\text{WO}_3\text{-ZrO}_2$ catalysts by Triwahyono et al. [46].

283

284 3.2 *n-C₇ Isomerization performance*

285

286 Fig. 7 depicts the isomerization activity of FSMO, $\text{MoO}_3/\text{KCC-1}$, Pt/FSMO, and
287 Pt/ $\text{MoO}_3/\text{KCC-1}$ in *n*-heptane isomerization within 200-350 $^\circ\text{C}$. Notably, all catalysts suffered
288 a decrement in the yield of isomers along with the rise in operating temperature, which attained
289 optimum yield at 200-250 $^\circ\text{C}$ and decreased above 250 $^\circ\text{C}$. This trend was associated with the
290 domination of cracking reaction compared to heptane isomerization at a higher temperature. It

291 is interesting to note that FSMO presented a superior *n*-heptane conversion (53-55%) and yield
292 of isomers (46-52%) compared to MoO₃/KCC-1, regardless of reaction temperature owing to
293 the considerably greater average pore size of FSMO (19.8 nm > 12.4 nm), as provided in Table
294 1. The enlargement in pore size was believed to minimize the transport restriction throughout
295 the catalysts as well as improve the diffusion steps [47, 48]. Additionally, the high
296 isomerization activity of FSMO than MoO₃/KCC-1 was probably related to possessing a
297 moderate amount of weak Brønsted acid sites. This finding is accorded with the result from
298 Py-IR with different outgassing temperatures (Fig. 4), which showed that FSMO possessed a
299 lower amount of Brønsted acid sites than KCC-1 supported MoO₃ catalysts since there was
300 more replacement of hydrogen atom (from Brønsted Si-OH) by Mo ions in forming Si-O-Mo
301 (Lewis acid sites). Consequently, this domination facilitated the formation of the protonic acid
302 site via H₂ dissociation and spillover, resulting in high isomerization activity. This trend was
303 also evident from the experimental work of Triwahyono et al. [4], in which the modification of
304 Y zeolite (HY) into fibrous silica@Y zeolite for C₅-C₇ isomerization.

305 Improvement in conversion and yield of isomer was noticed, especially at a lower
306 temperature (<350 °C) after incorporating Pt over FSMO and MoO₃/KCC-1 (Fig. 7). The
307 results demonstrated that Pt/FSMO achieved optimal conversion of 70.9% with 63.6% isomer
308 yield at a temperature of 250 °C. Instead, Pt/MoO₃/KCC-1 recorded a maximum conversion of
309 61.7% with the yield of an isomer of 56.5% at 200 °C. The enhancement in the isomerization
310 activity after Pt addition, especially at low temperatures, was plausibly attributed to the
311 considerably higher amount of Lewis acid sites than Brønsted and conjugated acid sites as
312 demonstrated in Py-IR (cf. Fig. 4), appropriately sufficient in generating protonic acid sites for
313 enriching the isomerization activity. Furthermore, this improvement could be linked to new
314 active site species generated from the interaction of Pt-support lattice defects [5]. Thus, the
315 addition of Pt over FSMO and MoO₃/KCC-1 could facilitate the activation of hydrogen

316 molecules via dissociation, enhancing the spillover process and thus enriching the formation
317 of protonic acid sites and hydrides for generating more isomer products. Interestingly, the yield
318 of cracking exhibited by Pt/FSMO is slightly lower compared to FSMO at 350 °C, suggesting
319 that Pt doped over FSMO effectively suppressed the binding interaction between FSMO and
320 atomic hydrogen, thus enriching the formation of hydride ions that are responsible for the
321 generation of the desired isomerization products [17]. In contrast, the high yield of cracking
322 witnessed at 350 °C for Pt/MoO₃/KCC-1 probably indicates that Pt incorporation could not
323 restrain the binding interaction between support and spillover hydrogen atom, thus lowering
324 the hydride generation. At low hydride availability, the hydrogen atoms' migration will occur
325 slowly compared to the β-fission, favouring more cracking products than isomers [49].

326 Increased isomerization activity with the incorporation of Pt is also consistent with
327 those of Al-Kandari et al. [50], who have evaluated the catalyst's isomerization activity over
328 TiO₂-supported MoO₃. They found that Pt incorporation effectively improved the bifunctional
329 metallic-acidic system of the MoO₃/TiO₂ catalyst, causing an improvement in *n*-heptane
330 isomerization activity at 573 K. In different work, Matsuda and coworkers [51] highlighted that
331 *n*-heptane isomerisation could be enhanced by introducing Pt over the reduced MoO₃ catalysts.
332 The authors noticed that this effort could produce acidic molybdenum oxyhydride (MoO_xH_y),
333 a crucial active site for enhancing the isomerization performance. Teh et al. [5] also discovered
334 a significant improvement in *n*-heptane isomerization after incorporating Pt on the MoO₃-
335 HBEA catalyst, accredited to the role of Pt in dissociating hydrogen molecule, suppressing the
336 MoO₃-spillover hydrogen atom interaction, while enriched protonic acid sites quantity.

337 The stability performance of Pt/FSMO and Pt/MoO₃/KCC-1 in *n*-heptane isomerization
338 under 28 h time-on-stream with intervals of 15 min for each dose was plotted in Fig. 8.
339 Although Pt/MoO₃/KCC-1 recorded superior conversion (>~60.0%) as compared to Pt/FSMO,
340 this catalyst experienced unsteady isomerization activity within 28 h reaction. This

341 phenomenon probably resulted from the high cracking side reaction, which could deactivate
342 the catalysts as a consequence of high coke accumulation. On the contrary, Pt/FSMO recorded
343 stable isomerization activity, especially with a better isomer yield (~48-52%) and a lower
344 cracking yield (<3.0%). The temperature-programmed oxidation analysis was conducted to
345 quantify the extent of carbonaceous deposition on the spent catalysts. As depicted in Fig. S1,
346 it was evidenced that Pt/FSMO possessed an inferior amount of coke compared to
347 Pt/MoO₃/KCC-1, further proving the stability of isomerization activity within 28 h reaction.
348 This trend proves the efficient role of Pt in enhancing the Lewis acid site of the catalyst for
349 generating essential protonic acid, minimizing the strong support-spillover hydrogen atom
350 interaction, and assisting in lessening the coke accumulation via hydrogenation. Thus, it is
351 noteworthy that Pt/FSMO catalysts have excellent potential for long-term isomerization
352 reactions.

353

354 3.4 Proposed reaction pathway

355

356 Based on the characterizations and *n*-heptane isomerization test, as mentioned before,
357 it can be evidenced that MoO₃ modification into the fibrous structure of support with silica
358 (FSMO), along with the incorporation of Pt element, could enrich the generation of Lewis acid
359 sites, thus, aiding in essential protonic acid sites generation at low temperature. This factor
360 further explains the excellent performance of Pt/FSMO catalyst on *n*-heptane isomerization at
361 a lower temperature. In order to comprehend the isomerization mechanism, the proposed
362 reaction pathway for *n*-heptane isomerization over Pt/FSMO is clarified in Fig. 9.

363 At the initial pathway, the pre-treatment of Pt/FSMO in the H₂ stream resulted in the
364 instigation of Pt-oxide into metallic Pt, the crucial hydrogen activation sites. The H₂ molecules
365 adsorbed on metallic Pt were further dissociated into two species of hydrogen atoms. This

366 dissociation step is crucial in isomerization since it contributes to acid site generation,
367 favouring the isomer generation instead of the cracking and polymerization of $n\text{-C}_7$ via β -
368 scission [4, 52]. After splitting, the produced hydrogen atom was spilt over onto the acidic
369 surface of FSMO and further diffused towards the Lewis acid sites. The spilt over of hydrogen
370 atoms then transferred an electron towards Lewis acid sites and bonded with Brønsted sites of
371 FSMO for forming protonic acid site (B-H^+ species). The generated protonic acid sites then
372 transferred protons to n -heptane, resulting in the formation of heptyl carbenium ion ($n\text{-C}_7^+$)
373 species. Afterwards, the accepted proton in the carbenium ion was moved along the
374 hydrocarbon chain, forming the iso-heptyl carbenium ion ($i\text{-C}_7^+$) species. Simultaneously, the
375 electron confined by the Lewis acid sites was further reacted with another split hydrogen atom
376 to become a hydride ion and attached to the Lewis acid site (L-H^-). Then, the produced L-H^-
377 species further interacted with $i\text{-C}_7^+$ species contributing to the generation of the desired
378 isomerization products. This proposed mechanism further proved that isomerization yield was
379 strongly influenced by the protonic acid sites and hydrate ions created from H_2 dissociation in
380 the presence of Pt. However, according to Hattori et al. [49], if there were excessive hydride
381 species during the reaction, the concentration of carbenium ions would considerably drop,
382 lowering the isomerization activity.

383

384 3.5 Comparative analysis

385

386 In order to evaluate the competency of our generated MoO_3 -based catalysts, a
387 comparative analysis (cf. Table 2) towards the reported MoO_3 -based catalyst's activity over n -
388 heptane isomerization was conducted. Fatah et al. [15] compared the isomerization activity of
389 over MoO_3 - and Pt- supported with MSN in the system consisting of H_2 or N_2 as the carrier.
390 The high performance of MoO_3 -supported with MSN conducted in the H_2 system was recorded

391 with mono- and di-branched iso-heptane, which yielded about 81.3 and 12.4%, respectively,
392 resulting from $(\text{MoO}_x)^-(\text{H}_y)^+$ active sites formation. On the other hand, the authors claimed that
393 the incompetence of the Pt- supported with MSN to generate protonic acid sites led to poor
394 isomerization activity. The author also evaluated the isomerization performance over MoO_3
395 supported by KCC-1, incorporating the phosphorous element [16]. The generation of $(\text{MoO}_x)^-$
396 $(\text{H}_y)^+$ active site along with the involvement of acidic centres from phosphorus inclusion and
397 MoO_3 , caused the improvement in the rate of n-heptane conversion.

398 In another effort, Ruslan et al. [53] investigated the role of the acid site of $\text{MoO}_3\text{-ZrO}_2$
399 catalysts toward n-heptane isomerization activity. Notably, the existence of the ZrO_2 tetragonal
400 phase in the catalysts contributed to enhancement in the number of Lewis acid sites, easing
401 active protonic acid site generation, thus responsible for the improvement of isomerization
402 activity and stability. Nevertheless, the authors witness superior cracking activity compared to
403 isomerization, which gradually increases with rising temperature from 300-400 °C. Besides,
404 Matsuda et al. [51] emphasized the acid site's role and its impact on isomerization performance
405 over $\text{Pt/MoO}_3\text{-SiO}_2$. They concluded that the isomerization selectivity of $\text{Pt/MoO}_3\text{-SiO}_2$ was
406 enhanced from 88.7-97.8% by raising the amount of MoO_3 employed from 20-100wt%, related
407 to the growth in the number of acid sites. Meanwhile, the cracking selectivity of $\text{Pt/MoO}_3\text{-SiO}_2$
408 was significantly reduced from 10.7% to 1.9% with the rising MoO_3 loading.

409 Liu et al. [54] stated that HBEA zeolite-supported molybdenum phosphide (MoP)
410 demonstrated superior isomerization selectivity (67.8%) compared to tungsten phosphide
411 supported on $\text{H}\beta$ (50.1%) and HMCM22 (64.2%). The authors also proposed that doping Ce,
412 Ni, and Cr elements over $\text{MoP/H}\beta$ substantially enriched the activity with Cr-promoted catalyst
413 promoted the superior isomerization selectivity around 73.1%, owing to the increment in the
414 density of strong acid sites of $\text{MoP/H}\beta$. Works by Sakagami et al. [11] and Parsafard et al. [55]
415 revealed a positive impact towards isomerization activity over MoO_3 and $\text{ZrO}_2\text{-HMS}$ catalysts,

416 respectively, accredited to the presence of Pt, which enhances protonic acid site generation via
417 H₂ dissociation and spillover phenomenon. This trend is in accordance with our findings.
418 However, the negative impact of Pt incorporation was experienced by Triwahyono et al. [46]
419 over MoO₃-ZrO₂. The authors justified that although Pt addition improved the hydrogen
420 adsorption rate, Pt addition has caused the intensification of Lewis acid sites instead of forming
421 more active protonic acid sites, consequently lowering the isomerization activity.

422 [Table 2](#) shows that our generated catalysts exhibited better or comparably to other
423 MoO₃-based catalysts utilized for the isomerization of n-heptane, especially in conversion and
424 isomerization selectivity. Indeed, the inferior cracking selectivity of studied catalysts compared
425 to the literature indicates that all generated catalysts are favoured to isomerization activity
426 compared to cracking. The outstanding performance of these generated catalysts, despite the
427 absence of Pt, is ascribed to the fibrous silica morphology, which contributes to the formation
428 of more Si-O-Mo for enriching Lewis acid sites quantity, causing growth in protonic acid sites
429 generation, hence, enhancing the isomerization activity. Moreover, after Pt was doped, the
430 enhancement of the Lewis acid site of the catalyst for generating essential protonic acid was
431 evidenced, assisting in suppressing the strong support-spillover hydrogen atom interaction and
432 lowering the coke accumulation. Thus, **isomerization** activity improved, especially at the lower
433 reaction temperature.

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435

436 **4.0 Conclusion**

437

438 This study appraised and compared the impact of Pt inclusion on physiochemical
439 characteristics and isomerization activity of synthesized MoO₃-based catalysts (FSMO and
440 MoO₃/KCC-1). XRD results indicated that the in-situ synthesis strategy effectively improved

441 the distribution of Mo particles in the Si framework than via incipient wetness impregnation.
442 Additionally, the in-situ synthesis strategy promotes Si-O-Mo formation, associated with the
443 alternately aligned SiO₂ and MoO₃ in the fibrous structure, strengthening MoO₃-SiO₂
444 interaction, as proved in FTIR analysis. Consequently, Py-IR analysis revealed that Lewis acid
445 sites intensity for FSMO was considerably higher than KCC-1 supported MoO₃ catalyst,
446 ascribed to the more replacement of -H (from Brønsted) by Mo ions in forming Si-O-Mo
447 (Lewis acid sites). Nevertheless, it is noteworthy that Pt inclusion over FSMO and MoO₃/KCC-
448 1 lessened those acid sites owing to the inevitable partial coverage by the Pt cluster.

449 The isomerization tests revealed enlargement in pore size, and the possession of a
450 moderate amount of weak Bronsted acid sites contributed to the superior n-heptane conversion
451 (53-55%) and yield of isomers (46-52%) for FSMO compared to MoO₃/KCC-1, regardless of
452 reaction temperature. Meanwhile, incorporating Pt over FSMO and MoO₃/KCC-1 improved
453 the conversion and yield of isomer, especially at a lower temperature (<350 °C), by achieving
454 optimal conversion of 70.9% with 63.6% isomer yield at a temperature of 250 °C. At the same
455 time, Pt/MoO₃/KCC-1 recorded a maximum conversion of 61.7% with the yield of an isomer
456 of 56.5% at 200 °C. This trend was plausibly accredited to the considerably more significant
457 amount of Lewis than Brønsted and conjugated acid sites, sufficient to generate protonic acid
458 sites for enriching the isomerization activity. Pt/FSMO recorded stable isomerization activity
459 within 28 h, with a better isomer yield and a lower cracking yield than Pt/MoO₃/KCC-1 due to
460 the efficient role of Pt in lessening the coke accumulation via hydrogenation. The findings of
461 this study demonstrated the potential of Pt/FSMO as the catalyst for isomerization reactions.

462

463 **Conflict of Interest**

464

465 The authors hereby declare no conflict of interest for the research work reported in this
466 manuscript.

467

468

469 **Authorship contribution**

470

471 **M.B. Bahari:** Project administration, Visualization, Writing - Original Draft, Methodology,

472 **A.A. Jalil:** Project administration, Funding acquisition, Conceptualization, Visualization,

473 Supervision, **N.S. Hassan:** Visualization, Writing - Original Draft, **MH Razak:** Investigation,

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485

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1 **Mechanistic studies of lower temperature isomerization of n-heptane over fibrous silica**
2 **molybdenum catalyst**

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27 **Abstract**

28

29 Platinum (Pt) inclusion on fibrous silica molybdenum (FSMo) and MoO₃/KCC-1 catalysts has
30 been prepared and utilized for the lower temperature (200-350 °C) catalytic isomerization of n-
31 heptane. The impact of Pt inclusion towards the structure, morphology, and acid distribution
32 of catalysts was characterized by XRD, FTIR, N₂-physisorption, Py-IR, and H₂-IR. Compared
33 with MoO₃/KCC-1, FSMo demonstrated superior MoO₃ dispersion and amount of Lewis acid
34 site associated with the in-situ synthesis technique. Although Pt inclusion slightly lessened acid
35 sites due to inevitable partial coverage by the Pt cluster, the considerably higher amount of
36 Lewis acid sites compared to Brønsted and conjugated sufficiently for generating protonic acid
37 sites for enriching the isomerization activity. In contrast to Pt/MoO₃/KCC-1 and undoped
38 catalysts, Pt/FSMO achieved a superior conversion of 70.9% with 63.6% isomer yield at a low
39 temperature of 250 °C. The 28-h stability tests demonstrated that Pt/FSMO recorded stable
40 isomerization activity, with a superior isomer yield (~48-52%) and inferior cracking yield
41 (<3.0%) than Pt/MoO₃/KCC-1.

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43 *Keywords:* n-C₇ isomerization; MoO₃-based catalysts; Platinum; Lewis acid; Protonic acid
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45 1.0 Introduction

46

47 Globally, comprehensive research and development initiatives have been undertaken to
48 produce clean gasoline with low aromatics, olefins, sulphur, and high-octane numbers, in
49 response to growing concerns over energy and environmental issues [1]. As a result, n-alkane
50 isomerization has gained popularity as a safe and environmentally friendly method for
51 enhancing gasoline quality [2]. This pathway allows n-alkanes with a linear carbon chain to be
52 converted into branched isomers with a high research octane number (RON) [3, 4]. So far,
53 tremendous effort has been put forth in researching light alkane isomerization since this
54 compound processing has been industrialised. Yet, this technique has not been utilized for *n*-
55 heptane and heavier alkanes due to the higher tendency of excessive development of cracking
56 products as the conversion rate increases, leading to the deactivation of the catalyst due to the
57 accumulation of coke on the surface's catalysts [5]. Hence, considering potential
58 implementation, it is critical to look for relatively efficient and selective catalysts for heavy *n*-
59 heptane isomerization while concurrently limiting cracking activities.

60 Bifunctional heterogeneous catalyst materials consisting of acidic supporting materials
61 as well as hydrogenation/hydrogenation metal sites are among the popular catalysts used for
62 the catalytic acid reaction [6, 7]. Both metallic and acidic functions influence the catalyst's
63 properties and facilitate the alkane hydro-conversion. For instance, metal sites could generate
64 carbonium ions via alkane dehydrogenation, a crucial intermediate species for initiating
65 isomerization and cracking [8]. Once the acidity of the catalyst is mild, and the
66 dehydrogenation activity of metal is substantial, a high yield of isomers is generated. In
67 addition, when the dehydrogenation activity is more significant, unsaturated products are more
68 hydrogenated, thus, inhibiting the escape acid-catalyzed skeleton rearrangement and cracking
69 [9]. Throughout the scientific literature, *n*-alkane isomerization has made considerable use of

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70 catalysts such as noble metals supported on microporous and mesoporous materials. In fact, it
71 was found that the hydrogen atom spillover mechanism used by bifunctional heterogeneous
72 catalysts could strongly induce isomerization [10]. Numerous acid-catalyzed reactions using
73 various types of catalysts, like Pt/MoO₃ [11-13], Pt/WO₃-ZrO₂ [14], MoO₃/MSN [15], and
74 Zn/HZSM-5 [10], have been explored for their spillover mechanisms.

75 Recently, the potential of the MoO₃ type catalysts has been extensively explored for a
76 wide range of catalytic processes like methanation, olefin metathesis, alcohols oxidation, and
77 isomerization accredited to MoO₃'s exceptional features, including excellent stability and
78 regeneration performance [16]. In addition, MoO₃ possessed both Lewis and Bronsted acid
79 sites, which is crucial for *n*-alkane isomerization and provides superior selectivity for heptane
80 isomerization compared to conventional catalysts. Incorporating second material as active sites
81 into bifunctional catalysts has aroused considerable attention in recent years owing to the
82 positive effects on isomerization performance, isomer selectivity, as well as stability. Second
83 Noble materials like Pd and Pt have been extensively studied, attributed to their hydrogen
84 spillover capability, boosting the isomerization activity. Indeed, the combination between Pt
85 and MoO₃ in a hydrogen atmosphere can generate several active species, including H_xMoO₃
86 and MoO₂, that are utilized for isomerization [11, 17]. Previous work has demonstrated that
87 incorporating Pt and MoO₃ into diverse supporting materials effectively improved *n*-heptane
88 isomerization performance [11, 13]. Regrettably, it should be noted that there is a paucity of
89 literature focusing on the usage of catalysts at low operating temperature.

90 Creating support with a dendrimer fibrous structure has recently received much
91 attention [18]. This strategy can produce an ideal support material possessing vast surface area,
92 tuneable pore volume, conveniently reachable inner surface, as well as superior thermal
93 stability [19-21]. In fact, this approach has resulted in a positive effect on the catalytic activity
94 of all catalytic pathways, including isomerization [4], methanation [22], cumene cracking [23],

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95 and dry reforming [24]. According to the researchers, the improvement was attributable to the
96 enhanced accessibility of active areas within this particular shape. Inspired by the previous
97 study, we synthesized fibrous silica-molybdenum trioxide (FSMo) supported platinum (Pt) and
98 assessed their capability in *n*-heptane isomerization at low reaction temperature for the first
99 time. The fibrous silica in the Pt/FSMo catalyst induces Si-O-Mo formation to enhance Lewis
100 acid site quantity, which will cause a growth in protonic acid site generation, thus enriching *n*-
101 heptane isomerization activity. The physicochemical features of the studied catalysts were
102 analysed in detail via XRD, N₂ physisorption and several in-situ IR analysis. The isomerization
103 pathway over Pt/FSMo catalyst is also elucidated.

104 105 106 **2.0 Experimental**

107 108 *2.1 MoO₃-based catalysts synthesis*

109
110 Fibrous silica-molybdenum (FSMo) and KCC-1 were prepared corresponding to the
111 microemulsion approach as detailed in the literature [25, 26]. In brief, a homogeneous solution
112 consisting of CTAB and urea was acquired by mixing and stirring both chemicals in distilled
113 water for 15 min (25°C). Thereafter, butanol, TEOS, and toluene were poured into the resulting
114 mixture under continuous agitation for one hour at ambient temperature. The mixture was
115 further agitated at ambient temperature for two hours to guarantee TEOS was hydrolyzed
116 entirely prior to the six-hour hydrothermal treatment in microwave irradiation (120 °C, 400 W).
117 Afterwards, the acquired solution was air-dried in an oven (24 h, 110 °C) to eradicate the
118 moisture before furnace-calcination (6 h, 550 °C) to gain desired FSMo. On the contrary, for
119 KCC-1 support production, TEOS was dropped along with butanol and toluene before being

120 treated with a similar condition for hydrothermal treatment, air-drying, and furnace-
121 calcination.

122 The incipient wetness impregnation technique, as reported by Siang et al. [27], was
123 applied in this work to generate Pt/FSMo and MoO₃/KCC-1 catalysts. For KCC-1 supported
124 MoO₃ catalyst, a calculated amount of ammonium heptamolybdate ([NH₄]₆Mo₇O₂₄) as the
125 metal precursor and KCC-1 support were separately dissolved in the deionized water prior to
126 the impregnation step. After both solutions were mixed and agitated at ambient temperature for
127 four hours, the resulting mixture was further air-dried in an oven (24 h, 110 °C) and
128 subsequently underwent furnace-calcination (6 h, 550 °C), which yielded MoO₃/KCC-1. A
129 similar approach as those stated earlier was employed to prepare Pt/FSMo using chloroplatinic
130 acid hexahydrate (H₂PtCl₆·6H₂O) as the metal precursor over FSMo support. For
131 Pt/MoO₃/KCC-1 catalyst preparation, the sequential incipient wetness impregnation technique
132 was employed by discretely dissolved H₂PtCl₆·6H₂O and as-synthesized MoO₃/KCC-1 in
133 deionized water. Afterwards, both dissolved materials were combined, agitated, dried, and
134 calcined, similar to those earlier impregnation steps to acquire Pt/MoO₃/KCC-1.

135

136 2.3 Characterizations of MoO₃-based catalysts

137

138 The crystalline structure of studied catalysts was assessed by X-ray diffractogram ($2\theta =$
139 $20-85^\circ$, step size = 0.02) on a Bruker Advance D8 diffractometer equipped with Cu Ka
140 radiation ($\lambda = 0.154$ nm, V = 40 kV, I = 40m A). The Barrett-Joyner-Halenda (BJH) and
141 Brunauer-Emmet-Teller (BET) techniques were applied to measure the catalyst's surface area
142 and pore properties using liquid nitrogen at -196°C in a Beckman Coulter SA3100 unit. The
143 one-hour-outgassed treatment was initially employed at 300°C prior to the nitrogen adsorption
144 at 77 K for eradicating the moisture and contaminants. The functional groups of the studied

145 catalysts were appraised via the FTIR-KBr approach at the range of 1600-400 cm⁻¹ with 5 cm⁻¹
146 resolutions on the FT-IR spectrometer unit (Agilent Cary 660). The acidity of studied catalysts
147 was scrutinized through Py-IR adsorption on stainless-steel cells with two CaF₂ windows
148 sealed. Initially, the tested catalysts were pelletized before exposing them to 4 Torr of pyridine
149 stream for a quarter-hour at 150 °C. Afterwards, the desorption of pyridine from tested catalysts
150 was carried out at a different temperature within 150-350°C. H₂-IR adsorption was also
151 operated in similar equipment for Py-IR adsorption. After activation treatment, the tested
152 catalysts were cooled down to room temperature before being subjected to 20 Torr of the
153 hydrogen stream under rising temperature up to 350 °C.

2.4 *n*-C₇ Isomerization evaluation

157 The micro-catalytic pulse reactor was utilized to evaluate *n*-heptane isomerization within
158 200-350 °C. About 0.2 g of the studied catalyst was employed in the reactor, followed by
159 exposure to the 100 ml min⁻¹ of O₂ stream (1 h, 400 °C) and then 100 ml min⁻¹ H₂ stream (3 h,
160 400 °C) as the pre-treatment step. Subsequently, the tested catalyst was cold down in a similar
161 H₂ stream to reach 150 °C. After stabilizing and reaching the necessary conditions, about two
162 μmol of *n*-C₅ was driven into the reactor filled with an H₂ stream (100 ml min⁻¹) to commence
163 the isomerization process. An online gas chromatograph (Agilent 6090N, FID, HP-5),
164 connected with a utilized micro-catalytic pulse reactor, scrutinized the isomerization product.
165 The isomerization product was confined using N₂ (77 K) before being flash-evaporated into
166 the gas chromatograph system. The isomerization activity was estimated based on the
167 conversion (*X*), yield (*Y*), and selectivity (*S*), as expressed in Eqs. (1)-(3).

$$168 \quad X_i(\%) = \frac{\sum C_i - C_{r,i}}{C_i} \times 100\% \quad (1)$$

$$S_i(\%) = \frac{C_i}{\sum C_i - C_{r,i}} \times 100\% \quad (2)$$

$$Y_i = \frac{X_i \times S_i}{100} \quad (3)$$

Where C_i = concentration for a specific product and $C_{r,i}$ = concentration of residual of n-heptane species, in weight percent unit.

3.0 Results and Discussion

3.1 Characterization analysis

XRD diffractograms for commercial MoO_3 and generated catalysts are shown in [Figs. 1A-B](#). All of the prepared catalysts showed a clear peak at $2\theta = 10^\circ$ - 70° on the plot. The XRD pattern of the MoO_3 catalyst demonstrated that it possesses an orthorhombic structure consistent with standard data (JCPDS Card No: 050508) [\[28\]](#). The crystallite peaks corresponded to the MoO_3 witnessed at an angle of 2θ about 12.9° (020), 23.4° (110), 25.8° (040), 27.4° (021), 33.7° (111), 39.0° (041), 46.1° (200), and 49.4° (002) in FSMo and $\text{MoO}_3/\text{KCC-1}$ [\[29\]](#). The inferior intensity of crystallite peaks of FSMo than $\text{MoO}_3/\text{KCC-1}$ catalyst, indicating that the in-situ synthesis strategy for generating FSMo promoted the well-distribution of Mo on the Si framework in comparison to $\text{MoO}_3/\text{KCC-1}$ prepared via the incipient wetness impregnation approach [\[30\]](#). Furthermore, due to the small size of the Pt species dispersed on the FSMo and $\text{MoO}_3/\text{KCC-1}$, possibly below than XRD detection limit, further explained for no visible diffraction peaks assignable to Pt species over Pt/FSMo and Pt/ $\text{MoO}_3/\text{KCC-1}$ [\[31\]](#).

192 The FTIR spectra (1400-400 cm^{-1}) of the functional groups owned by studied catalysts
193 are depicted in Fig. 2. Evidently, all the studied catalysts displayed five identical IR bands
194 ranging from 1095 cm^{-1} to 467 cm^{-1} . The absorption peaks appeared at a wavenumber of 1095
195 cm^{-1} , 956 cm^{-1} , 802 cm^{-1} , and 467 cm^{-1} are linked to the vibration of asymmetric Si-O-Si,
196 external Si-OH, symmetric Si-O-Si, and bending Si-O-Si, respectively [32]. Meanwhile,
197 absorption peaks identified at a wavenumber of 902 cm^{-1} overall studied catalysts signified
198 weak Mo=O vibration [33, 34]. Following the modification of MoO₃ into FSMO, a drop in the
199 intensity for the IR band at 956 cm^{-1} (external Si-OH vibration) for FSMO compared to
200 MoO₃/KCC-1 suggesting that more replacement of -H by Mo ions to form Si-O-Mo, associated
201 with the alternately aligned SiO₂ and MoO₃ in the fibrous structure. As a consequence, this
202 improvement could strengthen the interaction of MoO₃-SiO₂. This observation was also
203 reported by Sawal et al. [35] and Hitam et al. [36]. Remarkably, the FTIR spectrum of FSMO₃
204 was almost identical to that of Pt/FSMO₃, revealing no significant changes towards the silicate
205 framework of FSMO₃ after Pt incorporation. Apart from that, it is apparent from these FTIR
206 spectra that most of the IR bands for FSMO and MoO₃/KCC-1 catalysts experienced a slight
207 decrease in intensity compared to Pt-loaded catalysts, indicating the successful impregnation
208 of Pt over the tested catalysts, creating new interaction between Pt and SiO₂.

209 Further investigation was performed using N₂ physisorption analysis to examine
210 synthesized catalysts' textural properties; the results are presented in Fig. 3. As can be observed,
211 all the prepared catalysts demonstrated a type IV isotherm profile with a typical H3 hysteresis
212 loop, confirming the mesoporous structure characteristic of the synthesized catalysts (Fig. 3A)
213 [30]. In addition, in the absence of Pt element, both FSMo and MoO₃/KCC-1 catalysts
214 exhibited comparable N₂ uptakes. However, when Pt was loaded onto the catalyst surface, the
215 relative pressure of N₂ uptakes for Pt/MoO₃/KCC-1 increased substantially, while Pt/FSMo
216 catalyst demonstrated an insignificant change. This result may be explained by the fact that

217 high interaction between the Pt element and MoO₃ of Pt/MoO₃/KCC-1 reduced the pore
218 blockage of the MoO₃ on the mesopore of the KCC-1 [36]. Besides, the total pore volume for
219 MoO₃/KCC-1 catalyst was increased after adding Pt (Table 1) which indirectly supported the
220 statement mentioned earlier. Meanwhile, for Pt/FSMo catalyst, the pore volume was slightly
221 decreased compared to the FSMo catalyst, suggesting the filling of Pt inside the FSMo
222 mesopore [30].

223 Barrett-Joyner- Halenda (BJH) approach was applied to assess the average pore
224 diameter, as shown in Fig. 3B. The BJH pore size distribution demonstrated the pore diameter
225 of the synthesized catalysts placed within 3-40 (Å), showing the intrinsic of mesopores
226 features. It is worth noting that the pore distribution of FSMo and KCC-1 supported MoO₃
227 catalysts was considerably grown by adding Pt, probably due to the high mesoporous of Pt that
228 created inter-dendrimer distances [37]. For a better understanding of the textural properties of
229 as-prepared catalysts, the results were tabulated and presented in Table 1. As noticed, the
230 surface area for both FSMo (114.6 m²/g) and MoO₃/KCC-1 (221.3 m²/g) was reduced
231 considerably after adding Pt, suggesting that pores of FMSO and MoO₃/KCC-1 catalysts was
232 partially blocked by Pt particles [38]. This trend further inferred that the alteration of catalyst
233 structure could lead to surface area changes.

234 The efficacy of the isomerization reaction was considerably linked to the number and
235 intensity of the surface acidity in catalysts. Thus, Py-IR measurement was applied to assess the
236 distribution of Lewis and Brønsted acidic sites over activated catalysts at different temperatures
237 (150-250 °C), and the Py-IR spectra are illustrated in Fig. 4. As can be seen, all of the studied
238 catalysts disclosed three IR bands ranging within 1570-1420 cm⁻¹. It was noted that IR bands
239 spotted at 1454 cm⁻¹ and 1539 cm⁻¹ belonged to pyridinium ions adsorption on Lewis and
240 Brønsted acid sites, respectively [39, 40]. In addition, the appearance of IR band at a
241 wavenumber of 1488 cm⁻¹ over all tested catalysts related to Brønsted and Lewis acid sites

242 combination [41, 42]. Interestingly, by comparing FSMO and MoO₃/KCC-1, it was noticed
243 that Lewis acid sites intensity for FSMO was considerably higher than KCC-1 supported MoO₃
244 catalysts, possibly ascribed to the more replacement of -H (from Brønsted) by Mo ions in
245 forming Si-O-Mo (Lewis acid sites), resulted from the fibrous framework, in line with FTIR
246 finding. The decline in Lewis and Brønsted acid site intensity was witnessed after Pt was
247 impregnated onto FSMO and MoO₃/KCC-1, suggesting the inevitable partial coverage of
248 acidic sites by the Pt cluster. A comparable phenomenon was claimed by Setiabudi et al. [43]
249 and Teh et al. [5] during the isomerization over Ir/Pt-HZSM5 and Pt/MoO₃-HBEA catalysts,
250 respectively.

251 The impact of outgassed temperature (150-350 °C) towards the distribution of acidic
252 sites on studied catalysts is also elucidated in Fig. 4. The pyridine molecules adsorbed on weak
253 acid sites typically desorbed at a lower temperature whilst higher outgassing temperature is
254 required for desorbing pyridine molecules for strong acid sites. All tested catalysts appeared to
255 demonstrate intense interaction between pyridine and acidic sites at 150 °C and remained firm
256 at the outgassing temperature of 150 °C. The considerable decline in the intensity of acidic sites
257 for all studied catalysts was evidenced along with the rising outgassing temperature of up to
258 350 °C, signifying that weak-to-moderate Brønsted and Lewis acid sites are dominantly located
259 on those catalysts. This outcome also accords with the trends observed by other studies by
260 Fatah et al. [15] and Ma et al. [44] during the Py-IR evaluation over Pt/MSN, MoO₃/MSN, and
261 Al/SBA catalysts, respectively. Previous studies on isomerization have noted that the more
262 significant amount and intensity of acid sites of catalysts favour cracking instead of
263 isomerization reaction [5, 45]. Thus, the optimum amount with moderate acid sites is preferable
264 for enhanced isomerization.

265 Fig.5 disclosed the Py-IR spectra in the 1600-1400 cm⁻¹ when the pyridine pre-adsorbed
266 catalysts were heated in H₂ gas at elevated temperatures. The heating of all catalysts under H₂

267 gas exposure modified the intensity of Lewis and Bronsted acid sites at 1446 cm⁻¹ and 1538
268 cm⁻¹, respectively. Particularly, the intensity of Lewis acid sites declined with the simultaneous
269 rise in the Bronsted acid sites, indicating the formation of protonic acid sites from hydrogen
270 atoms spillover [4]. In general, protonic acid sites formed through interconversion of the Lewis
271 acid sites. In this study, the protonic acid site formation rate is higher in all catalysts at lower
272 temperatures (250-300 °C), as presented in Fig. 6. For FSMo and MoO₃/KCC-1, the formation
273 of protonic acid sites was probably due to the interaction of the Mo atom with the proton in the
274 form (MoO_x)-(H_y)⁺ that generated from releasing of the electron by atomic hydrogen, as
275 similarly reported by previous studies [15]. Interestingly, adding Pt into both catalysts
276 significantly increased the protonic acid site formation rate, especially at low operating
277 temperatures. These results indicated that Pt heightened the interaction of the hydrogen atom
278 with the surface of FSMo and MoO₃/KCC-1. This phenomenon has also been observed in
279 Pt/WO₃-ZrO₂ catalysts by Triwahyono et al. [46].

280

3.2 *n*-C₇ Isomerization performance

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283 Fig. 7 depicts the isomerization activity of FSMO, MoO₃/KCC-1, Pt/FSMO, and
284 Pt/MoO₃/KCC-1 in *n*-heptane isomerization within 200-350 °C. Notably, all catalysts suffered
285 a decrement in the yield of isomers along with the rise in operating temperature, which attained
286 optimum yield at 200-250 °C and decreased above 250 °C. This trend was associated with the
287 domination of cracking reaction compared to heptane isomerization at a higher temperature. It
288 is interesting to note that FSMO presented a superior *n*-heptane conversion (53-55%) and yield
289 of isomers (46-52%) compared to MoO₃/KCC-1, regardless of reaction temperature owing to
290 considerably greater average pore size of FSMO (19.8 nm > 12.4 nm), as provided in Table 1.
291 The enlargement in pore size was believed to minimize the transport restriction throughout the

292 catalysts as well as improve the diffusion steps [47, 48]. Additionally, the high isomerization
293 activity of FSMO than MoO₃/KCC-1 was probably related to possessing a moderate amount
294 of weak Bronsted acid sites. This finding is accorded with the result from Py-IR with different
295 outgassing temperatures (Fig. 4), which showed that FSMO possessed a lower amount of
296 Bronsted acid sites than KCC-1 supported MoO₃ catalysts since there was more replacement
297 of -H (from Brønsted) by Mo ions in forming Si-O-Mo (Lewis acid sites). Consequently, this
298 domination facilitated the formation of the protonic acid site via H₂ dissociation and spillover,
299 resulting in high isomerization activity. This trend was also evident from the experimental work
300 of Triwahyono et al. [4], in which the modification of Y zeolite (HY) into fibrous silica@Y
301 zeolite for C₅-C₇ isomerization.

302 Improvement in conversion and yield of isomer was noticed, especially at a lower
303 temperature (<350 °C) after incorporating Pt over FSMO and MoO₃/KCC-1 (Fig. 7). The
304 results demonstrated that Pt/FSMO achieved optimal conversion of 70.9% with 63.6% isomer
305 yield at a temperature of 250 °C. Instead, Pt/MoO₃/KCC-1 recorded a maximum conversion of
306 61.7% with the yield of an isomer of 56.5% at 200 °C. The enhancement in the isomerization
307 activity after Pt addition, especially at low temperatures, was plausibly attributed to the
308 considerably higher amount of Lewis acid sites than Brønsted and conjugated acid sites as
309 demonstrated in Py-IR (cf. Fig. 4), appropriately sufficient in generating protonic acid sites for
310 enriching the isomerization activity. Furthermore, this improvement could be linked to new
311 active site species generated from the interaction of Pt-support lattice defects [5]. Thus, the
312 addition of Pt over FSMO and MoO₃/KCC-1 could facilitate the activation of hydrogen
313 molecules via dissociation, enhancing the spillover process and thus enriching the formation
314 of protonic acid sites and hydrides for generating more isomer products. Interestingly, the yield
315 of cracking exhibited by Pt/FSMO is slightly lower compared to FSMO at 350 °C, suggesting
316 that Pt doped over FSMO effectively suppressed the binding interaction between FSMO and

1 317 atomic hydrogen, thus enriching the formation of hydride ions that are responsible for the
2 318 generation of the desired isomerization products [17]. In contrast, the high yield of cracking
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4 319 witnessed at 350 °C for Pt/MoO₃/KCC-1 probably indicates that Pt incorporation could not
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7 320 restrain the binding interaction between support and spillover hydrogen atom, thus lowering
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9 321 the hydride generation. At low hydride availability, the hydrogen atoms' migration will occur
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11 322 slowly compared to the β-fission, favouring more cracking products than isomers [49].
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14 323 Increased isomerization activity with the incorporation of Pt is also consistent with
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16 324 those of Al-Kandari et al. [50], who have evaluated the catalyst's isomerization activity over
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18 325 TiO₂-supported MoO₃. They found that Pt incorporation effectively improved the bifunctional
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20 326 metallic-acidic system of the MoO₃/TiO₂ catalyst, causing an improvement in *n*-heptane
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22 327 isomerization activity at 573 K. In different work, Matsuda and coworkers [51] highlighted that
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24 328 the enhancement of *n*-heptane isomerization could attain by introducing Pt over the reduce
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26 329 MoO₃ catalysts. The authors noticed that this effort could produce acidic molybdenum
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28 330 oxyhydride (MoO_xH_y), a crucial active site for enhancing the isomerization performance. Teh
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30 331 et al. [5] also discovered a significant improvement in *n*-heptane isomerization after
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32 332 incorporating Pt on the MoO₃-HBEA catalyst, accredited to the role of Pt in dissociating
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34 333 hydrogen molecule, suppressing the MoO₃-spillover hydrogen atom interaction, while enriched
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36 334 protonic acid sites quantity.
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44 335 The stability performance of Pt/FSMO and Pt/MoO₃/KCC-1 in *n*-heptane isomerization
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46 336 under 28 h time-on-stream with intervals of 15 min for each dose was plotted in Fig. 8.
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48 337 Although Pt/MoO₃/KCC-1 recorded superior conversion (>~60.0%) as compared to Pt/FSMO,
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50 338 this catalyst experienced unsteady isomerization activity within 28 h reaction. This
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52 339 phenomenon probably resulted from the high cracking side reaction, which could deactivate
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54 340 the catalysts as a consequence of high coke accumulation. On the contrary, Pt/FSMO recorded
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56 341 stable isomerization activity, especially with a better isomer yield (~48-52%) and a lower
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1 342 cracking yield (<3.0%). This trend proves the efficient role of Pt in enhancing the Lewis acid
2 343 site of the catalyst for generating essential protonic acid, minimizing the strong support-
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4 344 spillover hydrogen atom interaction, and assisting in lessening the coke accumulation via
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7 345 hydrogenation. Thus, it is noteworthy that Pt/FSMO catalysts have excellent potential for long-
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9 346 term isomerization reactions.

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14 348 3.4 Proposed reaction pathway

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19 350 Based on the characterizations and *n*-heptane isomerization test, as mentioned before,
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21 351 it can be evidenced that MoO₃ modification into the fibrous structure of support with silica
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23 352 (FSMO₃), along with the incorporation of Pt element, could enrich the generation of Lewis acid
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25 353 sites, thus, aiding in essential protonic acid sites generation at low temperature. This factor
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27 354 further explains the excellent performance of Pt/FSMO catalyst on *n*-heptane isomerization at
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29 355 a lower temperature. In order to comprehend the isomerization mechanism, the proposed
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31 356 reaction pathway for *n*-heptane isomerization over Pt/FSMO is clarified in Fig. 9.

36 357 At the initial pathway, the pre-treatment of Pt/FSMO in the H₂ stream resulted in the
37
38 358 instigation of Pt-oxide into metallic Pt, the crucial hydrogen activation sites. The H₂ molecules
39
40 359 adsorbed on metallic Pt were further dissociated into two species of hydrogen atoms. This
41
42 360 dissociation step is crucial in isomerization since it contributes to acid site generation,
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44 361 favouring the isomer generation instead of the cracking and polymerization of *n*-C₇ via β-
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46 362 scission [4, 52]. After splitting, the produced hydrogen atom was spilt over onto the acidic
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48 363 surface of FSMO and further diffused towards the Lewis acid sites. The spilt over of hydrogen
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50 364 atoms then transferred an electron towards Lewis acid sites and bonded with Brønsted sites of
51
52 365 FSMO for forming protonic acid site (B-H⁺ species). The generated protonic acid sites then
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54 366 transferred protons to *n*-heptane, resulting in the formation of heptyl carbenium ion (*n*-C₇⁺)

367 species. Afterwards, the accepted proton in the carbenium ion was moved along the
368 hydrocarbon chain, forming the iso-heptyl carbenium ion ($i\text{-C}_7^+$) species. Simultaneously, the
369 electron confined by the Lewis acid sites was further reacted with another split hydrogen atom
370 to become a hydride ion and attached to the Lewis acid site (L-H⁻). Then, the produced L-H⁻
371 species further interacted with $i\text{-C}_7^+$ species contributing to the generation of the desired
372 isomerization products. This proposed mechanism further proved that isomerization yield was
373 strongly influenced by the protonic acid sites and hydrate ions created from H₂ dissociation in
374 the presence of Pt. However, according to Hattori et al. [49], if there were excessive hydride
375 species during the reaction, the concentration of carbenium ions would considerably drop,
376 lowering the isomerization activity.

378 3.5 Comparative analysis

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380 In order to evaluate the competency of our generated MoO₃-based catalysts, a
381 comparative analysis (cf. Table 2) towards the reported MoO₃-based catalyst's activity over *n*-
382 heptane isomerization was conducted. Fatah et al. [15] compared the isomerization activity of
383 over MoO₃- and Pt- supported with MSN in the system consisting of H₂ or N₂ as the carrier.
384 The high performance of MoO₃-supported with MSN conducted in the H₂ system was recorded
385 with mono- and di-branched iso-heptane, which yielded about 81.3 and 12.4%, respectively,
386 resulting from (MoO_x)⁻(H_y)⁺ active sites formation. On the other hand, the authors claimed that
387 the incompetence of the Pt- supported with MSN to generate protonic acid sites led to poor
388 isomerization activity. The author also evaluated the isomerization performance over MoO₃
389 supported by KCC-1, incorporating the phosphorous element [16]. The generation of (MoO_x)⁻
390 (H_y)⁺ active site along with the involvement of acidic centres from phosphorus inclusion and
391 MoO₃, caused the improvement in the rate of *n*-heptane conversion.

392 In another effort, Ruslan et al. [53] investigated the role of the acid site of MoO₃-ZrO₂
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2 393 catalysts toward n-heptane isomerization activity. Notably, the existence of the ZrO₂ tetragonal
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5 394 phase in the catalysts contributed to enhancement in the number of Lewis acid sites, easing
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7 395 active protonic acid sites generation, thus responsible for the improvement of isomerization
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9 396 activity and stability. Nevertheless, the authors witness superior cracking activity compared to
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12 397 isomerization, which gradually increases with rising temperature from 300-400 °C. Besides,
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14 398 Matsuda et al. [51] emphasized the acid site's role and their impact on isomerization
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16 399 performance over Pt/MoO₃-SiO₂. They concluded that the isomerization selectivity of
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19 400 Pt/MoO₃-SiO₂ was enhanced from 88.7-97.8% by raising the amount of MoO₃ employed from
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22 401 20-100wt%, related to the growth in the number of acid sites. Meanwhile, the cracking
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24 402 selectivity of Pt/MoO₃-SiO₂ was significantly reduced from 10.7% to 1.9% with the rising
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26 403 MoO₃ loading.

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29 404 Liu et al. [54] stated that HBEA zeolite-supported molybdenum phosphide (MoP)
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31 405 demonstrated superior isomerization selectivity (67.8%) compared to tungsten phosphide
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33 406 supported on H β (50.1%) and HMCM22 (64.2%). The authors also proposed that doping Ce,
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36 407 Ni, and Cr elements over MoP/H β substantially enriched the activity with Cr-promoted catalyst
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39 408 promoted the superior isomerization selectivity around 73.1%, owing to the increment in the
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41 409 density of strong acid sites of MoP/H β . Works by Sakagami et al. [11] and Parsafard et al. [55]
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43 410 revealed a positive impact towards isomerization activity over MoO₃ and ZrO₂-HMS catalysts,
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45
46 411 respectively, accredited to the presence of Pt, which enhances protonic acid site generation via
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49 412 H₂ dissociation and spillover phenomenon. This trend is in accordance with our findings.
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51 413 However, the negative impact of Pt incorporation was experienced by Triwahyono et al. [46]
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53 414 over MoO₃-ZrO₂. The authors justified that although Pt addition improved the hydrogen
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56 415 adsorption rate, Pt addition has caused the intensification of Lewis acid sites instead of forming
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58 416 more active protonic acid sites, consequently lowering the isomerization activity.
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417 [Table 2](#) shows that our generated catalysts exhibited better or comparably to other
418 MoO₃-based catalysts that have been utilized for the isomerization of n-heptane, especially in
419 conversion and isomerization selectivity. Indeed, the inferior cracking selectivity of studied
420 catalysts compared to the literature indicates that all generated catalysts are favoured to
421 isomerization activity compared to cracking. The outstanding performance of these generated
422 catalysts, despite the absence of Pt, is ascribed to the fibrous silica morphology, which
423 contributes to the formation of more Si-O-Mo for enriching Lewis acid sites quantity, causing
424 growth in protonic acid sites generation, hence, enhancing the isomerization activity.
425 Moreover, after Pt was doped, the enhancement of the Lewis acid site of the catalyst for
426 generating essential protonic acid was evidenced, assisting in suppressing the strong support-
427 spillover hydrogen atom interaction and lowering the coke accumulation. Thus, isomerisation
428 activity improved, especially at the lower reaction temperature.

431 **4.0 Conclusion**

432
433 The impact of Pt inclusion towards physiochemical characteristics and isomerization
434 activity of synthesized MoO₃-based catalysts (FSMO and MoO₃/KCC-1) were appraised and
435 compared within this study. XRD results indicated that the in-situ synthesis strategy effectively
436 improved the distribution of Mo particles in the Si framework than via incipient wetness
437 impregnation. Additionally, the in-situ synthesis strategy promotes Si-O-Mo formation,
438 associated with the alternately aligned SiO₂ and MoO₃ in the fibrous structure, strengthening
439 MoO₃-SiO₂ interaction, as proved in FTIR analysis. Consequently, Py-IR analysis revealed that
440 Lewis acid sites intensity for FSMO was considerably higher than KCC-1 supported MoO₃
441 catalyst, ascribed to the more replacement of -H (from Brønsted) by Mo ions in forming Si-O-

442 Mo (Lewis acid sites). Nevertheless, it is noteworthy that Pt inclusion over FSMO and
443 MoO₃/KCC-1 lessened those acid sites owing to the inevitable partial coverage by the Pt
444 cluster.

445 The isomerization tests revealed enlargement in pore size, and the possession of a
446 moderate amount of weak Bronsted acid sites contributed to the superior n-heptane conversion
447 (53-55%) and yield of isomers (46-52%) for FSMO compared to MoO₃/KCC-1, regardless of
448 reaction temperature. Meanwhile, incorporating Pt over FSMO and MoO₃/KCC-1 improved
449 the conversion and yield of isomer, especially at a lower temperature (<350 °C), by achieving
450 optimal conversion of 70.9% with 63.6% isomer yield at a temperature of 250 °C. At the same
451 time, Pt/MoO₃/KCC-1 recorded a maximum conversion of 61.7% with the yield of an isomer
452 of 56.5% at 200 °C. This trend was plausibly accredited to the considerably greater amount of
453 Lewis than Brønsted and conjugated acid sites, which is sufficient to generate protonic acid
454 sites for enriching the isomerization activity. Pt/FSMO recorded stable isomerization activity
455 within 28 h, with a better isomer yield and a lower cracking yield than Pt/MoO₃/KCC-1 due to
456 the efficient role of Pt in lessening the coke accumulation via hydrogenation. The findings of
457 this study demonstrated the potential of Pt/FSMO as the catalyst for isomerization reactions.

458

459 **Conflict of Interest**

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461 The authors hereby declare no conflict of interest for the research work reported in this
462 manuscript.

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465 **Authorship contribution**

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1 467 **M.B. Bahari:** Project administration, Visualization, Writing - Original Draft, Methodology,
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3 468 **A.A. Jalil:** Project administration, Funding acquisition, Conceptualization, Visualization,
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1 **Mechanistic studies of lower temperature isomerization of n-heptane over fibrous silica**
2 **molybdenum catalyst**

3

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26

27 **Abstract**

28

29 Platinum (Pt) inclusion on fibrous silica molybdenum (FSMO) and MoO₃/KCC-1 catalysts has
30 been prepared and utilized for the lower temperature (200-350 °C) catalytic isomerization of n-
31 heptane. The impact of Pt inclusion towards the structure, morphology, and acid distribution
32 of catalysts was characterized by XRD, FTIR, N₂-physisorption, Py-IR, and H₂-IR. Compared
33 with MoO₃/KCC-1, FSMO demonstrated superior MoO₃ dispersion and amount of Lewis acid
34 site associated with the in-situ synthesis technique. Although Pt inclusion slightly lessened acid
35 sites due to inevitable partial coverage by the Pt cluster, the considerably higher amount of
36 Lewis acid sites compared to Brønsted and conjugated sufficiently for generating protonic acid
37 sites for enriching the isomerization activity. In contrast to Pt/MoO₃/KCC-1 and undoped
38 catalysts, Pt/FSMO achieved a superior conversion of 70.9% with 63.6% isomer yield at a low
39 temperature of 250 °C. The 28-h stability tests demonstrated that Pt/FSMO recorded stable
40 isomerization activity, with a superior isomer yield (~48-52%) and inferior cracking yield
41 (<3.0%) than Pt/MoO₃/KCC-1.

42

43 *Keywords:* n-C₇ isomerization; MoO₃-based catalysts; Platinum; Lewis acid; Protonic acid
44 side

45 1.0 Introduction

46

47 Globally, comprehensive research and development initiatives have been undertaken to
48 produce clean gasoline with low aromatics, olefins, sulphur, and high-octane numbers, in
49 response to growing concerns over energy and environmental issues [1]. As a result, n-alkane
50 isomerization has gained popularity as a safe and environmentally friendly method for
51 enhancing gasoline quality [2]. This pathway allows n-alkanes with a linear carbon chain to be
52 converted into branched isomers with a high research octane number (RON) [3, 4]. So far,
53 tremendous effort has been put forth in researching light alkane isomerization since this
54 compound processing has been industrialised. Yet, this technique has not been utilized for *n*-
55 heptane and heavier alkanes due to the higher tendency of excessive development of cracking
56 products as the conversion rate increases, leading to the deactivation of the catalyst due to the
57 accumulation of coke on the surface's catalysts [5]. Hence, considering potential
58 implementation, it is critical to look for relatively efficient and selective catalysts for heavy *n*-
59 heptane isomerization while concurrently limiting cracking activities.

60 Bifunctional heterogeneous catalyst materials consisting of acidic supporting materials
61 as well as hydrogenation/hydrogenation metal sites are among the popular catalysts used for
62 the catalytic acid reaction [6, 7]. Both metallic and acidic functions influence the catalyst's
63 properties and facilitate the alkane hydro-conversion. For instance, metal sites could generate
64 carbonium ions via alkane dehydrogenation, a crucial intermediate species for initiating
65 isomerization and cracking [8]. Once the acidity of the catalyst is mild, and the
66 dehydrogenation activity of metal is substantial, a high yield of isomers is generated. In
67 addition, when the dehydrogenation activity is more significant, unsaturated products are more
68 hydrogenated, thus, inhibiting the escape acid-catalyzed skeleton rearrangement and cracking
69 [9]. Throughout the scientific literature, *n*-alkane isomerization has made considerable use of

70 catalysts such as noble metals supported on microporous and mesoporous materials. In fact, it
71 was found that the hydrogen atom spillover mechanism used by bifunctional heterogeneous
72 catalysts could strongly induce isomerization [10]. Numerous acid-catalyzed reactions using
73 various types of catalysts, like Pt/MoO₃ [11-13], Pt/WO₃-ZrO₂ [14], MoO₃/MSN [15], and
74 Zn/HZSM-5 [10], have been explored for their spillover mechanisms.

75 Recently, the potential of the MoO₃ type catalysts has been extensively explored for a
76 wide range of catalytic processes like methanation, olefin metathesis, alcohols oxidation, and
77 isomerization accredited to MoO₃'s exceptional features, including excellent stability and
78 regeneration performance [16]. In addition, MoO₃ possessed both Lewis and Bronsted acid
79 sites, which is crucial for *n*-alkane isomerization and provides superior selectivity for heptane
80 isomerization compared to conventional catalysts. Incorporating second material as active sites
81 into bifunctional catalysts has aroused considerable attention in recent years owing to the
82 positive effects on isomerization performance, isomer selectivity, as well as stability. Second
83 Noble materials like Pd and Pt have been extensively studied, attributed to their hydrogen
84 spillover capability, boosting the isomerization activity. Indeed, the combination between Pt
85 and MoO₃ in a hydrogen atmosphere can generate several active species, including H_xMoO₃
86 and MoO₂, that are utilized for isomerization [11, 17]. Previous work has demonstrated that
87 incorporating Pt and MoO₃ into diverse supporting materials effectively improved *n*-heptane
88 isomerization performance [11, 13]. Regrettably, it should be noted that there is a paucity of
89 literature focusing on the usage of catalysts at low operating temperature.

90 Creating support with a dendrimer fibrous structure has recently received much
91 attention [18]. This strategy can produce an ideal support material possessing vast surface area,
92 tuneable pore volume, conveniently reachable inner surface, as well as superior thermal
93 stability [19-21]. In fact, this approach has resulted in a positive effect on the catalytic activity
94 of all catalytic pathways, including isomerization [4], methanation [22], cumene cracking [23],

95 and dry reforming [24]. According to the researchers, the improvement was attributable to the
96 enhanced accessibility of active areas within this particular shape. Inspired by the previous
97 study, we synthesized fibrous silica-molybdenum trioxide (FSMO) supported platinum (Pt)
98 and assessed their capability in *n*-heptane isomerization at low reaction temperature for the first
99 time. The fibrous silica in the Pt/FSMO catalyst induces Si-O-Mo formation to enhance Lewis
100 acid site quantity, which will cause a growth in protonic acid site generation, thus enriching *n*-
101 heptane isomerization activity. The physicochemical features of the studied catalysts were
102 analysed in detail via XRD, N₂ physisorption and several in-situ IR analysis. The isomerization
103 pathway over Pt/FSMO catalyst is also elucidated.

104

105

106 **2.0 Experimental**

107

108 *2.1 MoO₃-based catalysts synthesis*

109

110 Fibrous silica-molybdenum (FSMO) and KCC-1 were prepared corresponding to the
111 microemulsion approach as detailed in the literature [25, 26]. In brief, a homogeneous solution
112 consisting of CTAB and urea was acquired by mixing and stirring both chemicals in distilled
113 water for 15 min (25°C). Thereafter, butanol and toluene were poured into the mixture under
114 continuous agitation at ambient temperature before being dopped with the specified amount of
115 MoO₃ seed. The resulting mixture was further agitated at ambient temperature for two hours to
116 guarantee TEOS was hydrolyzed entirely prior to the six-hour hydrothermal treatment in
117 microwave irradiation (120 °C, 400 W). Afterwards, the acquired solution was air-dried in an
118 oven (24 h, 110 °C) to eradicate the moisture before furnace-calcination (6 h, 550 °C) to gain
119 desired FSMO. On the contrary, for KCC-1 support production, TEOS was dropped along with

120 butanol and toluene before being treated with a similar condition for hydrothermal treatment,
121 air-drying, and furnace-calcination.

122 The incipient wetness impregnation technique, as reported by Siang et al. [27], was
123 applied in this work to generate Pt/FSMO and MoO₃/KCC-1 catalysts. For KCC-1 supported
124 10.0 wt% MoO₃ catalyst, a calculated amount of ammonium heptamolybdate ([NH₄]₆Mo₇O₂₄)
125 as the metal precursor and KCC-1 support were separately dissolved in the deionized water
126 prior to the impregnation step. After both solutions were mixed and agitated at ambient
127 temperature for four hours, the resulting mixture was further air-dried in an oven (24 h, 110
128 °C) and subsequently underwent furnace-calcination (6 h, 550 °C), which yielded MoO₃/KCC-
129 1. A similar approach as those stated earlier was employed to prepare Pt/FSMO using
130 chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) as the metal precursor (0.1 wt%Pt) over
131 FSMO support. For Pt/MoO₃/KCC-1 catalyst preparation, the sequential incipient wetness
132 impregnation technique was employed by discretely dissolved H₂PtCl₆·6H₂O and as-
133 synthesized MoO₃/KCC-1 in deionized water. Afterwards, both dissolved materials were
134 combined, agitated, dried, and calcined, similar to those earlier impregnation steps to acquire
135 Pt/MoO₃/KCC-1.

136

137 2.3 Characterizations of MoO₃-based catalysts

138

139 The crystalline structure of studied catalysts was assessed by X-ray diffractogram ($2\theta =$
140 $20-85^\circ$, step size = 0.02) on a Bruker Advance D8 diffractometer equipped with Cu Ka
141 radiation ($\lambda = 0.154$ nm, V = 40 kV, I = 40m A). The Barrett-Joyner-Halenda (BJH) and
142 Brunauer-Emmet-Teller (BET) techniques were applied to measure the catalyst's surface area
143 and pore properties using liquid nitrogen at -196 °C in a Beckman Coulter SA3100 unit. The
144 one-hour-outgassed treatment was initially employed at 300 °C prior to the nitrogen adsorption

145 at 77 K for eradicating the moisture and contaminants. The functional groups of the studied
146 catalysts were appraised via the FTIR-KBr approach at the range of 1600-400 cm^{-1} with 5 cm^{-1}
147 resolutions on the FT-IR spectrometer unit (Agilent Cary 660). The acidity of studied catalysts
148 was scrutinized through Py-IR adsorption on stainless-steel cells with two CaF_2 windows
149 sealed. Initially, the tested catalysts were pelletized before exposing them to 4 Torr of pyridine
150 stream for a quarter-hour at 150 °C. Afterwards, the desorption of pyridine from tested catalysts
151 was carried out at a different temperature within 150-350°C. H_2 -IR adsorption was also
152 operated in similar equipment for Py-IR adsorption. After activation treatment, the tested
153 catalysts were cooled to room temperature before being subjected to 20 Torr of the hydrogen
154 stream under rising temperature up to 350 °C. Temperature-programmed oxidation (TPO) was
155 carried out in Mettler Toledo TGA/SDTA/851e Thermo-gravimetric unit to estimate the
156 carbonaceous deposition on the surface of spent catalysts within the temperature of 10-900 °C.

157

158 2.4 *n-C₇ Isomerization evaluation*

159

160 The micro-catalytic pulse reactor was utilized to evaluate *n*-heptane isomerization within
161 200-350 °C. About 0.2 g of the studied catalyst was employed in the reactor, followed by
162 exposure to the 100 ml min^{-1} of O_2 stream (1 h, 400 °C) and then 100 ml min^{-1} H_2 stream (3 h,
163 400 °C) as the pre-treatment step. Subsequently, the tested catalyst was cold down in a similar
164 H_2 stream to reach 150 °C. After stabilizing and reaching the necessary conditions, about two
165 μmol of *n-C₇* was driven into the reactor filled with an H_2 stream (100 ml min^{-1}) to commence
166 the isomerization process. An online gas chromatograph (Agilent 6090N, FID, HP-5),
167 connected with a utilized micro-catalytic pulse reactor, scrutinized the isomerization product.
168 The isomerization product was confined using N_2 (-196 °C) before being flash-evaporated into

169 the gas chromatograph system. The isomerization activity was estimated based on the
170 conversion (X), yield (Y), and selectivity (S), as expressed in Eqs. (1)-(3).

$$171 \quad X_i(\%) = \frac{\sum A_i - A_{r,i}}{\sum A_i} \times 100\% \quad (1)$$

$$172 \quad S_i(\%) = \frac{A_i}{\sum A_i - A_{r,i}} \times 100\% \quad (2)$$

$$173 \quad Y_i = \frac{X_i \times S_i}{100} \quad (3)$$

174 Where A_i = corrected chromatographic area for a specific product and $A_{r,i}$ = corrected
175 chromatographic area for residual of n-heptane species, in weight percent unit.

176

177

178 **3.0 Results and Discussion**

179

180 *3.1 Characterization analysis*

181

182 XRD diffractograms for commercial MoO_3 and generated catalysts are shown in [Figs.](#)
183 [1A-B](#). All of the prepared catalysts showed a clear peak at $2\theta = 10^\circ$ - 70° on the plot. The
184 XRD pattern of the MoO_3 catalyst demonstrated that it possesses an orthorhombic structure
185 consistent with standard data (JCPDS Card No: 050508) [\[28\]](#). The crystallite peaks
186 corresponded to the MoO_3 witnessed at an angle of 2θ about 12.9° (020), 23.4° (110), 25.8°
187 (040), 27.4° (021), 33.7° (111), 39.0° (041), 46.1° (200), and 49.4° (002) in FSMO and
188 $\text{MoO}_3/\text{KCC-1}$ [\[29\]](#). The inferior intensity of crystallite peaks of FSMO than $\text{MoO}_3/\text{KCC-1}$
189 catalyst, indicating that the in-situ synthesis strategy for generating FSMO promoted the well-
190 distribution of Mo on the Si framework in comparison to $\text{MoO}_3/\text{KCC-1}$ prepared via the
191 incipient wetness impregnation approach [\[30\]](#). Furthermore, due to the small size of the Pt

192 species dispersed on the FSMO and MoO₃/KCC-1, possibly below than XRD detection limit,
193 further explained for no visible diffraction peaks assignable to Pt species over Pt/FSMO and
194 Pt/ MoO₃/KCC-1 [31].

195 The FTIR spectra (1400-400 cm⁻¹) of the functional groups owned by studied catalysts
196 are depicted in Fig. 2. Evidently, all the studied catalysts displayed five identical IR bands
197 ranging from 1095 cm⁻¹ to 467 cm⁻¹. The absorption peaks appeared at a wavenumber of 1095
198 cm⁻¹, 956 cm⁻¹, 802 cm⁻¹, and 467 cm⁻¹ are linked to the vibration of asymmetric Si-O-Si,
199 external Si-OH, symmetric Si-O-Si, and bending Si-O-Si, respectively [32]. Meanwhile,
200 absorption peaks identified at a wavenumber of 902 cm⁻¹ overall studied catalysts signified
201 weak Mo=O vibration [33, 34]. Following the modification of MoO₃ into FSMO, a drop in the
202 intensity for the IR band at 956 cm⁻¹ (external Si-OH vibration) for FSMO compared to
203 MoO₃/KCC-1 suggesting that more replacement of hydrogen atom by Mo ions to form Si-O-
204 Mo, associated with the alternately aligned SiO₂ and MoO₃ in the fibrous structure. As a
205 consequence, this improvement could strengthen the interaction of MoO₃-SiO₂. This
206 observation was also reported by Sawal et al. [35] and Hitam et al. [36]. Remarkably, the FTIR
207 spectrum of FSMO was almost identical to that of Pt/FSMO, revealing no significant changes
208 towards the silicate framework of FSMO after Pt incorporation. Apart from that, it is apparent
209 from these FTIR spectra that most of the IR bands for FSMO and MoO₃/KCC-1 catalysts
210 experienced a slight decrease in intensity compared to Pt-loaded catalysts, indicating the
211 successful impregnation of Pt over the tested catalysts, creating new interaction between Pt and
212 SiO₂.

213 Further investigation was performed using N₂ physisorption analysis to examine
214 synthesized catalysts' textural properties; the results are presented in Fig. 3. As can be observed,
215 all the prepared catalysts demonstrated a type IV isotherm profile with a typical H3 hysteresis
216 loop, confirming the mesoporous structure characteristic of the synthesized catalysts (Fig. 3A)

217 [30]. In addition, in the absence of Pt element, both FSMO and MoO₃/KCC-1 catalysts
218 exhibited comparable N₂ uptakes. However, when Pt was loaded onto the catalyst surface, the
219 N₂ uptakes for Pt/MoO₃/KCC-1 increased substantially at higher relative pressure, while
220 Pt/FSMO catalyst demonstrated an insignificant change. This result may be explained by the
221 fact that high interaction between the Pt element and MoO₃ of Pt/MoO₃/KCC-1 reduced the
222 pore blockage of the MoO₃ on the mesopore of the KCC-1 [36]. Besides, the total pore volume
223 for MoO₃/KCC-1 catalyst increased after adding Pt (Table 1), which indirectly supported the
224 earlier statement. Meanwhile, for Pt/FSMO catalyst, the pore volume was slightly decreased
225 compared to the FSMO catalyst, suggesting the filling of Pt inside the FSMO mesopore [30].

226 Barrett-Joyner- Halenda (BJH) approach was applied to assess the average pore
227 diameter, as shown in Fig. 3B. The BJH pore size distribution demonstrated the pore diameter
228 of the synthesized catalysts placed within 3-40 (Å), showing the intrinsic of mesopores
229 features. It is worth noting that the pore distribution of FSMO and KCC-1-supported MoO₃
230 catalysts were considerably grown by adding Pt, probably due to the high mesoporous of Pt
231 that created inter-dendrimer distances [37]. For a better understanding of the textural properties
232 of as-prepared catalysts, the results were tabulated and presented in Table 1. As noticed, the
233 surface area for both FSMO (114.6 m²/g) and MoO₃/KCC-1 (221.3 m²/g) was reduced
234 considerably after adding Pt, suggesting that pores of FSMO and MoO₃/KCC-1 catalysts were
235 partially blocked by Pt particles [38]. This trend further inferred that the alteration of catalyst
236 structure could lead to surface area changes.

237 The efficacy of the isomerization reaction was considerably linked to the number and
238 intensity of the surface acidity in catalysts. Thus, Py-IR measurement was applied to assess the
239 distribution of Lewis and Brønsted acidic sites over activated catalysts at different temperatures
240 (150-250 °C), and the Py-IR spectra are illustrated in Fig. 4. As can be seen, all of the studied
241 catalysts disclosed three IR bands ranging within 1570-1420 cm⁻¹. It was noted that IR bands

242 spotted at 1454 cm^{-1} and 1539 cm^{-1} belonged to pyridinium ions adsorption on Lewis and
243 Brønsted acid sites, respectively [39, 40]. In addition, the appearance of IR band at a
244 wavenumber of 1488 cm^{-1} over all tested catalysts related to Brønsted and Lewis acid sites
245 combination [41, 42]. Interestingly, by comparing FSMO and $\text{MoO}_3/\text{KCC-1}$, it was noticed
246 that Lewis acid sites intensity for FSMO was considerably higher than KCC-1 supported MoO_3
247 catalysts, possibly ascribed to the more replacement of -H (from Brønsted) by Mo ions in
248 forming Si-O-Mo (Lewis acid sites), resulted from the fibrous framework, in line with FTIR
249 finding. The decline in Lewis and Brønsted acid site intensity was witnessed after Pt was
250 impregnated onto FSMO and $\text{MoO}_3/\text{KCC-1}$, suggesting the inevitable partial coverage of
251 acidic sites by the Pt cluster. A comparable phenomenon was claimed by Setiabudi et al. [43]
252 and Teh et al. [5] during the isomerization over Ir/Pt-HZSM5 and Pt/ MoO_3 -HBEA catalysts,
253 respectively.

254 The impact of outgassed temperature ($150\text{-}350\text{ }^\circ\text{C}$) towards the distribution of acidic
255 sites on studied catalysts is also elucidated in Fig. 4. The pyridine molecules adsorbed on weak
256 acid sites typically desorbed at a lower temperature whilst higher outgassing temperature is
257 required for desorbing pyridine molecules for strong acid sites. All tested catalysts appeared to
258 demonstrate intense interaction between pyridine and acidic sites at $150\text{ }^\circ\text{C}$ and remained firm
259 at the outgassing temperature of $150\text{ }^\circ\text{C}$. The considerable decline in the intensity of acidic sites
260 for all studied catalysts was evidenced along with the rising outgassing temperature of up to
261 $350\text{ }^\circ\text{C}$, signifying that weak-to-moderate Brønsted and Lewis acid sites are dominantly located
262 on those catalysts. This outcome also accords with the trends observed by other studies by
263 Fatah et al. [15] and Ma et al. [44] during the Py-IR evaluation over Pt/MSN, MoO_3/MSN , and
264 Al/SBA catalysts, respectively. Previous studies on isomerization have noted that the more
265 significant amount and intensity of acid sites of catalysts favour cracking instead of

266 isomerization reaction [5, 45]. Thus, the optimum amount with moderate acid sites is preferable
267 for enhanced isomerization.

268 Fig.5 disclosed the Py-IR spectra in 1600-1400 cm^{-1} when the pyridine pre-adsorbed
269 catalysts were heated in H_2 gas at elevated temperatures. The heating of all catalysts under H_2
270 gas exposure modified the intensity of Lewis and Bronsted acid sites at 1446 cm^{-1} and 1538
271 cm^{-1} , respectively. Particularly, the intensity of Lewis acid sites declined with the simultaneous
272 rise in the Bronsted acid sites, indicating the formation of protonic acid sites from hydrogen
273 atoms spillover [4]. In general, protonic acid sites formed through interconversion of the Lewis
274 acid sites. In this study, the protonic acid site formation rate is higher in all catalysts at lower
275 temperatures (250-300 $^\circ\text{C}$), as presented in Fig. 6. For FSMO and $\text{MoO}_3/\text{KCC-1}$, the formation
276 of protonic acid sites was probably due to the interaction of the Mo atom with the proton in the
277 form $(\text{MoO}_x)\text{-(H}_y\text{)}^+$ that generated from releasing of the electron by atomic hydrogen, as
278 similarly reported by previous studies [15]. Interestingly, adding Pt into both catalysts
279 significantly increased the protonic acid site formation rate, especially at low operating
280 temperatures. These results indicated that Pt heightened the interaction of the hydrogen atom
281 with the surface of FSMO and $\text{MoO}_3/\text{KCC-1}$. This phenomenon has also been observed in
282 $\text{Pt}/\text{WO}_3\text{-ZrO}_2$ catalysts by Triwahyono et al. [46].

283

284 3.2 *n-C₇ Isomerization performance*

285

286 Fig. 7 depicts the isomerization activity of FSMO, $\text{MoO}_3/\text{KCC-1}$, Pt/FSMO , and
287 $\text{Pt}/\text{MoO}_3/\text{KCC-1}$ in *n*-heptane isomerization within 200-350 $^\circ\text{C}$. Notably, all catalysts suffered
288 a decrement in the yield of isomers along with the rise in operating temperature, which attained
289 optimum yield at 200-250 $^\circ\text{C}$ and decreased above 250 $^\circ\text{C}$. This trend was associated with the
290 domination of cracking reaction compared to heptane isomerization at a higher temperature. It

291 is interesting to note that FSMO presented a superior *n*-heptane conversion (53-55%) and yield
292 of isomers (46-52%) compared to MoO₃/KCC-1, regardless of reaction temperature owing to
293 the considerably greater average pore size of FSMO (19.8 nm > 12.4 nm), as provided in [Table](#)
294 [1](#). The enlargement in pore size was believed to minimize the transport restriction throughout
295 the catalysts as well as improve the diffusion steps [\[47, 48\]](#). Additionally, the high
296 isomerization activity of FSMO than MoO₃/KCC-1 was probably related to possessing a
297 moderate amount of weak Brønsted acid sites. This finding is accorded with the result from
298 Py-IR with different outgassing temperatures ([Fig. 4](#)), which showed that FSMO possessed a
299 lower amount of Brønsted acid sites than KCC-1 supported MoO₃ catalysts since there was
300 more replacement of hydrogen atom (from Brønsted Si-OH) by Mo ions in forming Si-O-Mo
301 (Lewis acid sites). Consequently, this domination facilitated the formation of the protonic acid
302 site via H₂ dissociation and spillover, resulting in high isomerization activity. This trend was
303 also evident from the experimental work of Triwahyono et al. [\[4\]](#), in which the modification of
304 Y zeolite (HY) into fibrous silica@Y zeolite for C₅-C₇ isomerization.

305 Improvement in conversion and yield of isomer was noticed, especially at a lower
306 temperature (<350 °C) after incorporating Pt over FSMO and MoO₃/KCC-1 ([Fig. 7](#)). The
307 results demonstrated that Pt/FSMO achieved optimal conversion of 70.9% with 63.6% isomer
308 yield at a temperature of 250 °C. Instead, Pt/MoO₃/KCC-1 recorded a maximum conversion of
309 61.7% with the yield of an isomer of 56.5% at 200 °C. The enhancement in the isomerization
310 activity after Pt addition, especially at low temperatures, was plausibly attributed to the
311 considerably higher amount of Lewis acid sites than Brønsted and conjugated acid sites as
312 demonstrated in Py-IR (cf. [Fig. 4](#)), appropriately sufficient in generating protonic acid sites for
313 enriching the isomerization activity. Furthermore, this improvement could be linked to new
314 active site species generated from the interaction of Pt-support lattice defects [\[5\]](#). Thus, the
315 addition of Pt over FSMO and MoO₃/KCC-1 could facilitate the activation of hydrogen

316 molecules via dissociation, enhancing the spillover process and thus enriching the formation
317 of protonic acid sites and hydrides for generating more isomer products. Interestingly, the yield
318 of cracking exhibited by Pt/FSMO is slightly lower compared to FSMO at 350 °C, suggesting
319 that Pt doped over FSMO effectively suppressed the binding interaction between FSMO and
320 atomic hydrogen, thus enriching the formation of hydride ions that are responsible for the
321 generation of the desired isomerization products [17]. In contrast, the high yield of cracking
322 witnessed at 350 °C for Pt/MoO₃/KCC-1 probably indicates that Pt incorporation could not
323 restrain the binding interaction between support and spillover hydrogen atom, thus lowering
324 the hydride generation. At low hydride availability, the hydrogen atoms' migration will occur
325 slowly compared to the β -fission, favouring more cracking products than isomers [49].

326 Increased isomerization activity with the incorporation of Pt is also consistent with
327 those of Al-Kandari et al. [50], who have evaluated the catalyst's isomerization activity over
328 TiO₂-supported MoO₃. They found that Pt incorporation effectively improved the bifunctional
329 metallic-acidic system of the MoO₃/TiO₂ catalyst, causing an improvement in *n*-heptane
330 isomerization activity at 573 K. In different work, Matsuda and coworkers [51] highlighted that
331 *n*-heptane isomerisation could be enhanced by introducing Pt over the reduced MoO₃ catalysts.
332 The authors noticed that this effort could produce acidic molybdenum oxyhydride (MoO_xH_y),
333 a crucial active site for enhancing the isomerization performance. Teh et al. [5] also discovered
334 a significant improvement in *n*-heptane isomerization after incorporating Pt on the MoO₃-
335 HBEA catalyst, accredited to the role of Pt in dissociating hydrogen molecule, suppressing the
336 MoO₃-spillover hydrogen atom interaction, while enriched protonic acid sites quantity.

337 The stability performance of Pt/FSMO and Pt/MoO₃/KCC-1 in *n*-heptane isomerization
338 under 28 h time-on-stream with intervals of 15 min for each dose was plotted in Fig. 8.
339 Although Pt/MoO₃/KCC-1 recorded superior conversion (>~60.0%) as compared to Pt/FSMO,
340 this catalyst experienced unsteady isomerization activity within 28 h reaction. This

341 phenomenon probably resulted from the high cracking side reaction, which could deactivate
342 the catalysts as a consequence of high coke accumulation. On the contrary, Pt/FSMO recorded
343 stable isomerization activity, especially with a better isomer yield (~48-52%) and a lower
344 cracking yield (<3.0%). The temperature-programmed oxidation analysis was conducted to
345 quantify the extent of carbonaceous deposition on the spent catalysts. As depicted in [Fig. S1](#),
346 it was evidenced that Pt/FSMO possessed an inferior amount of coke compared to
347 Pt/MoO₃/KCC-1, further proving the stability of isomerization activity within 28 h reaction.
348 This trend proves the efficient role of Pt in enhancing the Lewis acid site of the catalyst for
349 generating essential protonic acid, minimizing the strong support-spillover hydrogen atom
350 interaction, and assisting in lessening the coke accumulation via hydrogenation. Thus, it is
351 noteworthy that Pt/FSMO catalysts have excellent potential for long-term isomerization
352 reactions.

353

354 3.4 Proposed reaction pathway

355

356 Based on the characterizations and *n*-heptane isomerization test, as mentioned before,
357 it can be evidenced that MoO₃ modification into the fibrous structure of support with silica
358 (FSMO), along with the incorporation of Pt element, could enrich the generation of Lewis acid
359 sites, thus, aiding in essential protonic acid sites generation at low temperature. This factor
360 further explains the excellent performance of Pt/FSMO catalyst on *n*-heptane isomerization at
361 a lower temperature. In order to comprehend the isomerization mechanism, the proposed
362 reaction pathway for *n*-heptane isomerization over Pt/FSMO is clarified in [Fig. 9](#).

363 At the initial pathway, the pre-treatment of Pt/FSMO in the H₂ stream resulted in the
364 instigation of Pt-oxide into metallic Pt, the crucial hydrogen activation sites. The H₂ molecules
365 adsorbed on metallic Pt were further dissociated into two species of hydrogen atoms. This

366 dissociation step is crucial in isomerization since it contributes to acid site generation,
367 favouring the isomer generation instead of the cracking and polymerization of $n\text{-C}_7$ via β -
368 scission [4, 52]. After splitting, the produced hydrogen atom was spilt over onto the acidic
369 surface of FSMO and further diffused towards the Lewis acid sites. The spilt over of hydrogen
370 atoms then transferred an electron towards Lewis acid sites and bonded with Brønsted sites of
371 FSMO for forming protonic acid site (B-H^+ species). The generated protonic acid sites then
372 transferred protons to n -heptane, resulting in the formation of heptyl carbenium ion ($n\text{-C}_7^+$)
373 species. Afterwards, the accepted proton in the carbenium ion was moved along the
374 hydrocarbon chain, forming the iso-heptyl carbenium ion ($i\text{-C}_7^+$) species. Simultaneously, the
375 electron confined by the Lewis acid sites was further reacted with another split hydrogen atom
376 to become a hydride ion and attached to the Lewis acid site (L-H^-). Then, the produced L-H^-
377 species further interacted with $i\text{-C}_7^+$ species contributing to the generation of the desired
378 isomerization products. This proposed mechanism further proved that isomerization yield was
379 strongly influenced by the protonic acid sites and hydrate ions created from H_2 dissociation in
380 the presence of Pt. However, according to Hattori et al. [49], if there were excessive hydride
381 species during the reaction, the concentration of carbenium ions would considerably drop,
382 lowering the isomerization activity.

383

384 3.5 Comparative analysis

385

386 In order to evaluate the competency of our generated MoO_3 -based catalysts, a
387 comparative analysis (cf. Table 2) towards the reported MoO_3 -based catalyst's activity over n -
388 heptane isomerization was conducted. Fatah et al. [15] compared the isomerization activity of
389 over MoO_3 - and Pt- supported with MSN in the system consisting of H_2 or N_2 as the carrier.
390 The high performance of MoO_3 -supported with MSN conducted in the H_2 system was recorded

391 with mono- and di-branched iso-heptane, which yielded about 81.3 and 12.4%, respectively,
392 resulting from $(\text{MoO}_x)^-(\text{H}_y)^+$ active sites formation. On the other hand, the authors claimed that
393 the incompetence of the Pt- supported with MSN to generate protonic acid sites led to poor
394 isomerization activity. The author also evaluated the isomerization performance over MoO_3
395 supported by KCC-1, incorporating the phosphorous element [16]. The generation of $(\text{MoO}_x)^-$
396 $(\text{H}_y)^+$ active site along with the involvement of acidic centres from phosphorus inclusion and
397 MoO_3 , caused the improvement in the rate of n-heptane conversion.

398 In another effort, Ruslan et al. [53] investigated the role of the acid site of $\text{MoO}_3\text{-ZrO}_2$
399 catalysts toward n-heptane isomerization activity. Notably, the existence of the ZrO_2 tetragonal
400 phase in the catalysts contributed to enhancement in the number of Lewis acid sites, easing
401 active protonic acid site generation, thus responsible for the improvement of isomerization
402 activity and stability. Nevertheless, the authors witness superior cracking activity compared to
403 isomerization, which gradually increases with rising temperature from 300-400 °C. Besides,
404 Matsuda et al. [51] emphasized the acid site's role and its impact on isomerization performance
405 over $\text{Pt/MoO}_3\text{-SiO}_2$. They concluded that the isomerization selectivity of $\text{Pt/MoO}_3\text{-SiO}_2$ was
406 enhanced from 88.7-97.8% by raising the amount of MoO_3 employed from 20-100wt%, related
407 to the growth in the number of acid sites. Meanwhile, the cracking selectivity of $\text{Pt/MoO}_3\text{-SiO}_2$
408 was significantly reduced from 10.7% to 1.9% with the rising MoO_3 loading.

409 Liu et al. [54] stated that HBEA zeolite-supported molybdenum phosphide (MoP)
410 demonstrated superior isomerization selectivity (67.8%) compared to tungsten phosphide
411 supported on $\text{H}\beta$ (50.1%) and HMCM22 (64.2%). The authors also proposed that doping Ce,
412 Ni, and Cr elements over $\text{MoP/H}\beta$ substantially enriched the activity with Cr-promoted catalyst
413 promoted the superior isomerization selectivity around 73.1%, owing to the increment in the
414 density of strong acid sites of $\text{MoP/H}\beta$. Works by Sakagami et al. [11] and Parsafard et al. [55]
415 revealed a positive impact towards isomerization activity over MoO_3 and $\text{ZrO}_2\text{-HMS}$ catalysts,

416 respectively, accredited to the presence of Pt, which enhances protonic acid site generation via
417 H₂ dissociation and spillover phenomenon. This trend is in accordance with our findings.
418 However, the negative impact of Pt incorporation was experienced by Triwahyono et al. [46]
419 over MoO₃-ZrO₂. The authors justified that although Pt addition improved the hydrogen
420 adsorption rate, Pt addition has caused the intensification of Lewis acid sites instead of forming
421 more active protonic acid sites, consequently lowering the isomerization activity.

422 [Table 2](#) shows that our generated catalysts exhibited better or comparably to other
423 MoO₃-based catalysts utilized for the isomerization of n-heptane, especially in conversion and
424 isomerization selectivity. Indeed, the inferior cracking selectivity of studied catalysts compared
425 to the literature indicates that all generated catalysts are favoured to isomerization activity
426 compared to cracking. The outstanding performance of these generated catalysts, despite the
427 absence of Pt, is ascribed to the fibrous silica morphology, which contributes to the formation
428 of more Si-O-Mo for enriching Lewis acid sites quantity, causing growth in protonic acid sites
429 generation, hence, enhancing the isomerization activity. Moreover, after Pt was doped, the
430 enhancement of the Lewis acid site of the catalyst for generating essential protonic acid was
431 evidenced, assisting in suppressing the strong support-spillover hydrogen atom interaction and
432 lowering the coke accumulation. Thus, isomerization activity improved, especially at the lower
433 reaction temperature.

434

435

436 **4.0 Conclusion**

437

438 This study appraised and compared the impact of Pt inclusion on physiochemical
439 characteristics and isomerization activity of synthesized MoO₃-based catalysts (FSMO and
440 MoO₃/KCC-1). XRD results indicated that the in-situ synthesis strategy effectively improved

441 the distribution of Mo particles in the Si framework than via incipient wetness impregnation.
442 Additionally, the in-situ synthesis strategy promotes Si-O-Mo formation, associated with the
443 alternately aligned SiO₂ and MoO₃ in the fibrous structure, strengthening MoO₃-SiO₂
444 interaction, as proved in FTIR analysis. Consequently, Py-IR analysis revealed that Lewis acid
445 sites intensity for FSMO was considerably higher than KCC-1 supported MoO₃ catalyst,
446 ascribed to the more replacement of -H (from Brønsted) by Mo ions in forming Si-O-Mo
447 (Lewis acid sites). Nevertheless, it is noteworthy that Pt inclusion over FSMO and MoO₃/KCC-
448 1 lessened those acid sites owing to the inevitable partial coverage by the Pt cluster.

449 The isomerization tests revealed enlargement in pore size, and the possession of a
450 moderate amount of weak Bronsted acid sites contributed to the superior n-heptane conversion
451 (53-55%) and yield of isomers (46-52%) for FSMO compared to MoO₃/KCC-1, regardless of
452 reaction temperature. Meanwhile, incorporating Pt over FSMO and MoO₃/KCC-1 improved
453 the conversion and yield of isomer, especially at a lower temperature (<350 °C), by achieving
454 optimal conversion of 70.9% with 63.6% isomer yield at a temperature of 250 °C. At the same
455 time, Pt/MoO₃/KCC-1 recorded a maximum conversion of 61.7% with the yield of an isomer
456 of 56.5% at 200 °C. This trend was plausibly accredited to the considerably more significant
457 amount of Lewis than Brønsted and conjugated acid sites, sufficient to generate protonic acid
458 sites for enriching the isomerization activity. Pt/FSMO recorded stable isomerization activity
459 within 28 h, with a better isomer yield and a lower cracking yield than Pt/MoO₃/KCC-1 due to
460 the efficient role of Pt in lessening the coke accumulation via hydrogenation. The findings of
461 this study demonstrated the potential of Pt/FSMO as the catalyst for isomerization reactions.

462

463 **Conflict of Interest**

464

465 The authors hereby declare no conflict of interest for the research work reported in this
466 manuscript.

467

468

469 **Authorship contribution**

470

471 **M.B. Bahari:** Project administration, Visualization, Writing - Original Draft, Methodology,

472 **A.A. Jalil:** Project administration, Funding acquisition, Conceptualization, Visualization,

473 Supervision, **N.S. Hassan:** Visualization, Writing - Original Draft, **MH Razak:** Investigation,

474 Formal analysis, **N.M. Izzudin:** Investigation, Formal analysis, **NF. Khusnun:** Visualization,

475 Writing - Original Draft, **M.A.H. Aziz:** Investigation, Formal analysis, **A.F.A. Rahman:**

476 Investigation, Formal analysis, **W. Nabgan:** Investigation, Formal analysis, **Saravanan**

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479

480 **Acknowledgement**

481

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648

List of Tables

Mechanistic studies of lower temperature isomerization of n-heptane over fibrous silica molybdenum catalyst

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Table 1 Textural properties of catalysts

Catalyst	Surface area (m²/g)	Pore volume x10⁻³ (cm³/g)	Average pore size (nm)
FSMO	114.6	5.2	19.8
Pt/FSMO	101.3	3.8	21.4
MoO ₃ /KCC-1	221.3	9.1	12.4
Pt/MoO ₃ /KCC-1	208.8	9.8	16.4

Table 2: Catalytic performance of MoO₃-based catalysts for *n*-heptane isomerization

Catalyst	T (°C)	Conversion (%)	Isomer selectivity (%)		Isomer Yield (%)	Cracking selectivity (%)	Ref.
			Mono-branched	Di-branched			
MoO ₃ /MSN	350	45.0	81.3	12.4	43.4	3.5	[15]
MoO ₃ /KCC-1	300	45.8	52.6	24.0	39.7	23.4	[16]
P/MoO ₃ /KCC-1	300	67.4	50.2	28.5	53.0	21.3	
Pt/MoO ₃ -SiO ₂	250	57.3	97.5		-	2.1	[51]
MoO ₃ -ZrO ₂	400	31.0	44.7		-	55.3	[53]
MoP/HMCM22	300	13.7	58.4	5.8	8.8	30.5	[54]
MoP/Hβ-40%	300	18.0	56.7	11.1	12.2	20.1	
Pt/MoO ₃	300	53.1	90.9		-	9.1	[11]
Pt/Na-MoO ₃	300	50.3	94.6		-	5.4	
Pt/Zr(x)-HMS	300	39.2	22.4	18.0	-	59.5	[55]
Pt-MoO _x /ZrO ₂ -HMS	300	53.1	43.6	22.8	-	33.6	
MoO ₃ -ZrO ₂	300	-	44.7	-	13.8	-	[46]
Pt/MoO ₃ -ZrO ₂	300	-	0	-	0	-	
FSMO	300	53.0	58.1	32.5	48.0	0.5	This work
Pt/FSMO	300	56.8	60.1	27.9	50.0	0.2	
MoO ₃ /KCC-1	300	47.5	61.4	25.5	41.2	0.5	
Pt/MoO ₃ /KCC-1	300	53.1	66.9	19.7	46.0	0.4	

List of Figures

Mechanistic studies of lower temperature isomerization of *n*-heptane over fibrous silica molybdenum catalyst

M.B. Bahari^c, A.A. Jalil^{a,b*}, C.R. Mamat^c, N.S. Hassan^{a,b}, M.H. Razak^a, N.M. Izzudin^a, M.A.A. Aziz^a, N.F. Khusnun^b, M.A.H. Aziz^c, A.F.A. Rahman^b, W. Nabgan^d, Saravanan Rajendran^e

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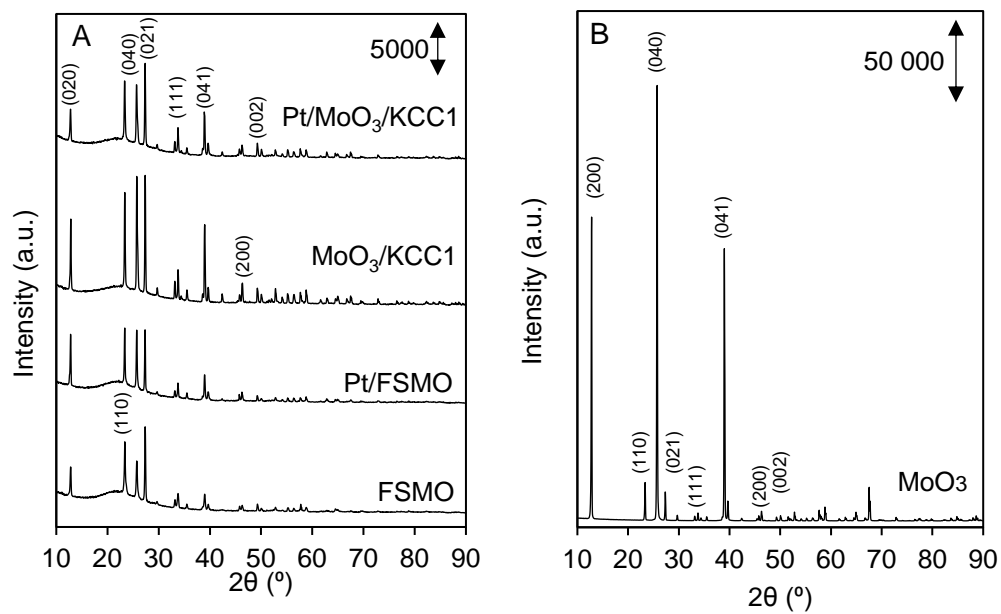


Fig. 1 XRD diffractogram for (A) MoO₃-based catalysts and (B) commercial MoO₃

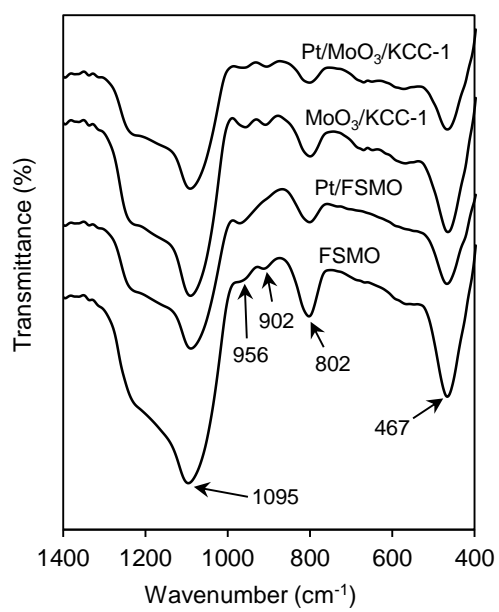


Fig. 2 FTIR spectra for all catalysts

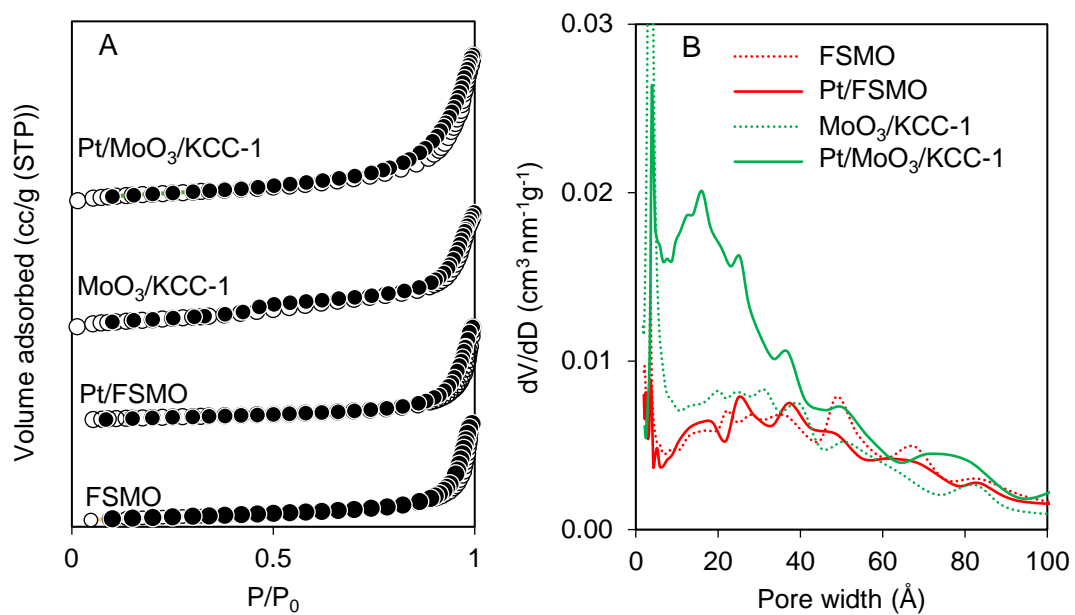


Fig. 3 N₂ adsorption-desorption and pore distribution for MoO₃-based catalysts

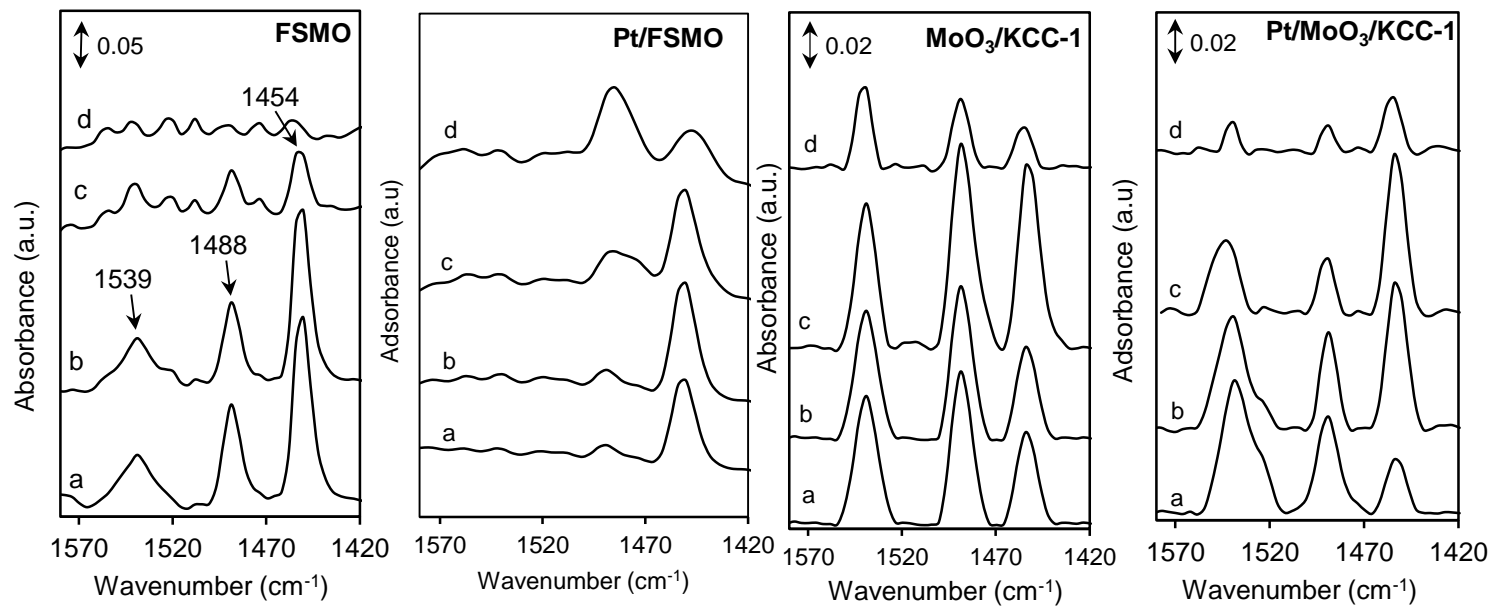


Fig 4 FTIR spectra of catalysts (a) after pyridine adsorption at 150 °C, then outgassing at (b) 150 °C (c) 250 °C (d) 350 °C

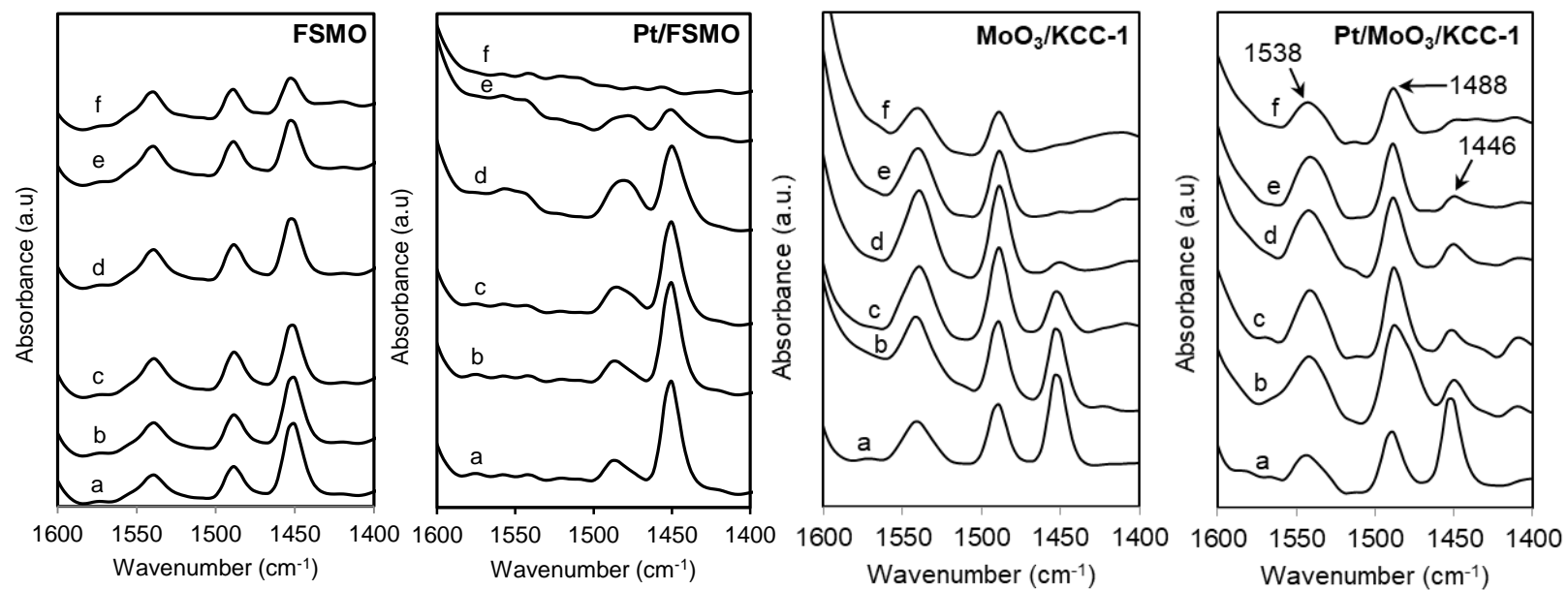


Fig. 5 Py-IR spectra of studied catalysts. Spectral variations induced by heating the pyridine-adsorbed sample in H₂ at (a) room temperature (b) 100 °C (c) 200 °C (d) 250 °C (e) 300 °C (f) 350 °C

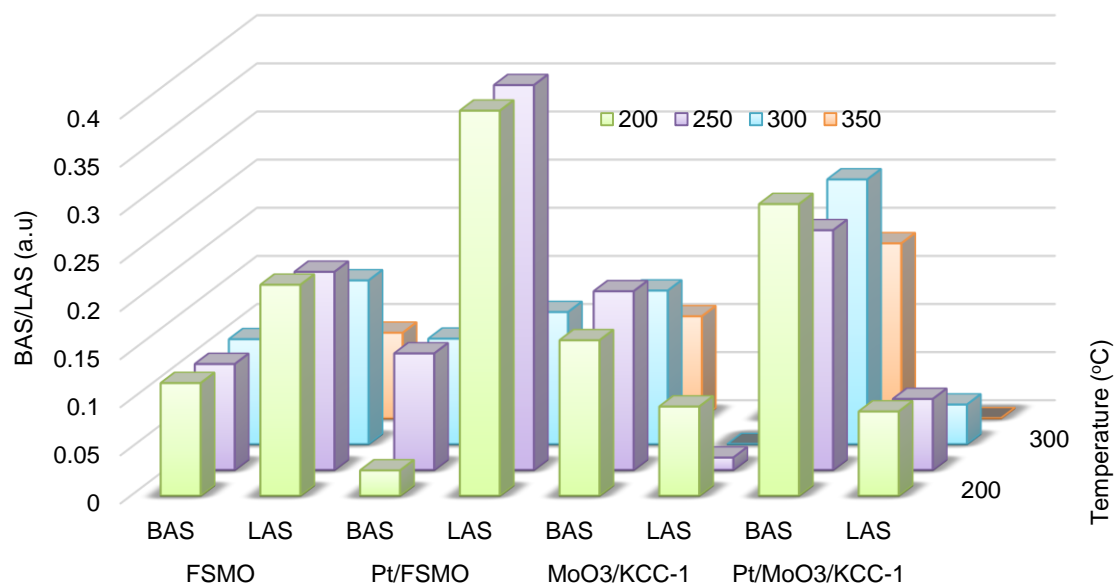


Fig. 6 Acid sites distribution of MoO₃-based catalysts detected by IR pyridine-preadsorbed and heated in hydrogen at elevated temperature (200-350°C)

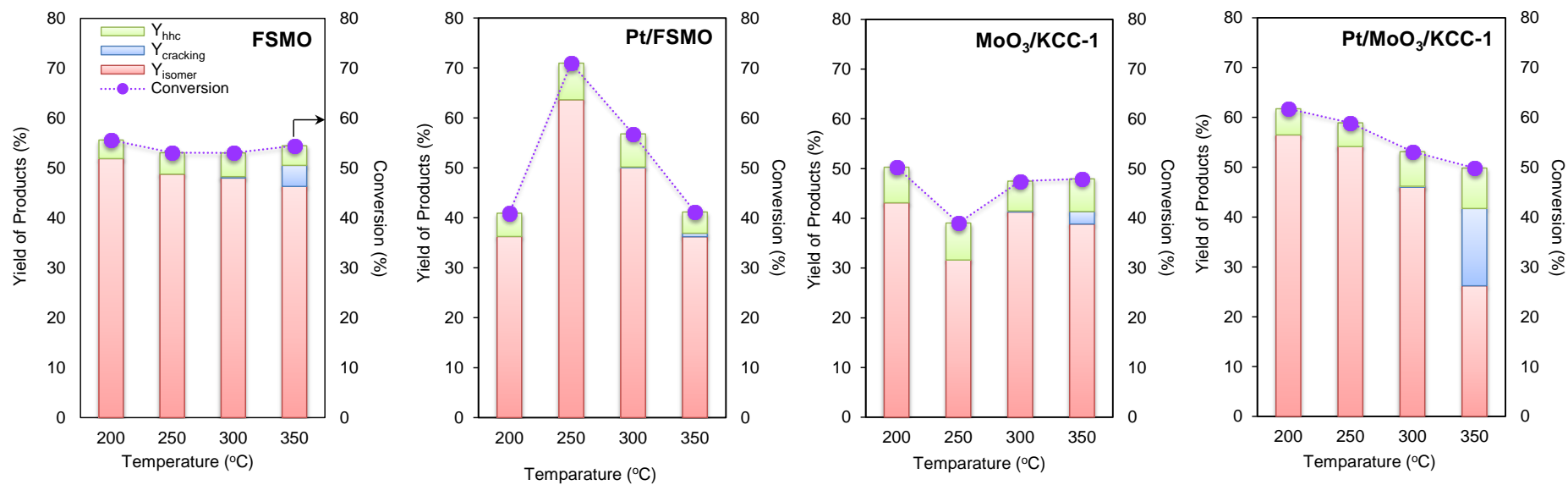


Fig. 7 *n*-heptane isomerization activity over MoO_3 -based catalyst at elevated temperature (Y_{iso} = yield of isomer, $Y_{cracking}$ = Yield of cracking, and Y_{hhc} = Yield of higher hydrocarbon)

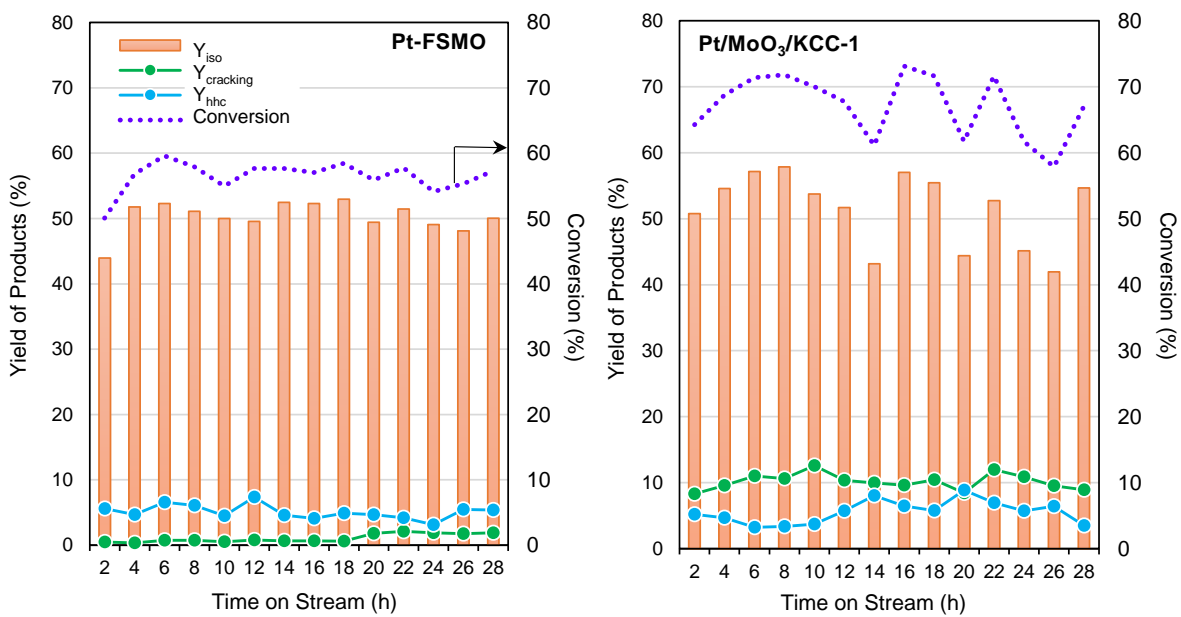


Fig. 8 Catalyst stability test under 28 h time-on-stream at 250 °C, atmospheric pressure, and 0.2 g of catalyst. (2 μmol of n-C₇ + 100 ml min⁻¹ H₂)

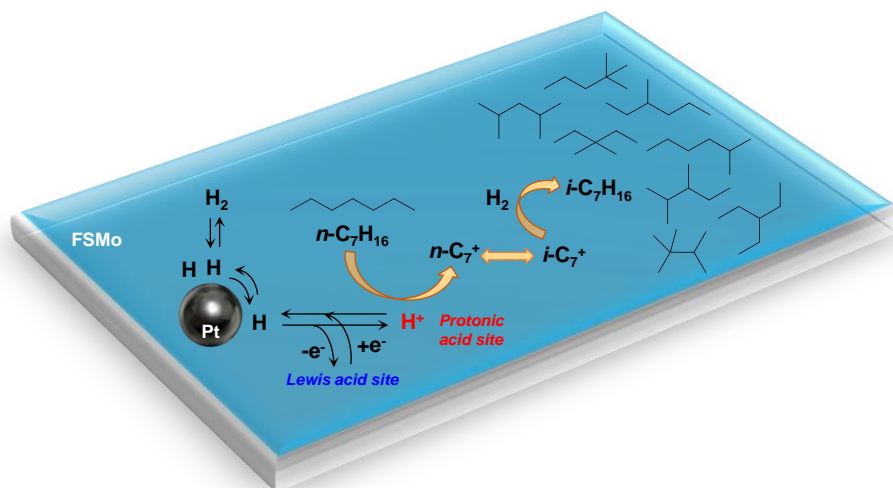


Fig. 9 Mechanism proposed for n-heptane isomerization over **Pt/FSMO**



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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: