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EFFECT OF SUPPORT ON MOLYBDENUM OXIDE ACIDITY FOR N-HEPTANE ISOMERIZATION

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Graphical abstract
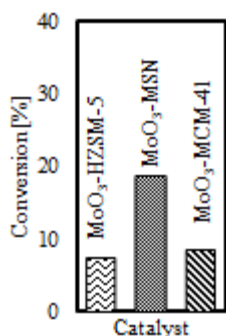
Abstract

Skeletal isomerization of alkanes into the corresponding branched isomers has attracted many attentions as a reaction to produce clean fuel with high octane quality. In this study, molybdenum oxide (MoO_3) catalyst supported on mesostructured silica nanoparticles (MSN), HZSM-5 and MCM-41 activity were being tested towards *n*-heptane isomerization at 623 K. The catalyst acidity was characterized by using FTIR pre-adsorb pyridine. The results showed that MoO_3-MSN possesses highest Lewis acid and lowest Brönsted acid concentrations. The catalytic testing towards *n*-heptane isomerization showed that MoO_3-MSN exhibited the highest *n*-heptane conversion of 18.7 % at 623 K. It was suggested that the high Lewis acid in the MoO_3-MSN may facilitate the formation of active protonic acid sites from molecular hydrogen through hydrogen spillover mechanism and hence improves the *n*-heptane conversion.

Keywords: Molybdenum oxide, pyridine, Lewis acid, protonic acid site, *n*-heptane isomerization

Abstrak

Proses isomerisasi alkana berangka lurus kepada alkana berangka bercabang telah menarik banyak perhatian di dalam usaha untuk menghasilkan bahan api bersih dengan nilai oktana yang tinggi. Di dalam kajian ini, aktiviti pemangkin molibdena oksida disokong dengan mesostruktur silika nanopartikel (MSN), HZSM-5 dan MCM-41 telah diuji terhadap pengisomeriran *n*-heptana pada suhu 623 K. Ciri keasidan pemangkin telah dikaji menggunakan FTIR pra-jerap piridina. Hasil kajian menunjukkan bahawa MoO_3-MSN mempunyai kepakatan asid Lewis tertinggi dan kepekatan Bronsted asid terendah berbanding pemangkin lain. Ujian pemangkin terhadap isomerisasi heptane menunjukkan MoO_3-MSN mempunyai penukaran n-heptana tertinggi sebanyak 18.7 % pada suhu 623 K. Nilai keasidan Lewis yang tinggi dalam MoO_3-MSN menjurus kepada proses pembentukan tapak asid protonik aktif daripada molekul hidrogen melalui mekanisma limpahan hidrogen dan seterusnya meningkatkan kadar penukaran n-heptana.

Kata kunci: Molibdina oksida, piridina, asid Lewis, asid protonik, pengisomeran *n*-heptana

1.0 INTRODUCTION

Nowadays, demand for the synthesis of clean gasoline with high research octane number (RON) and low contents of aromatics such as benzene is growing due to several issues of environmental concern [1]. Octane number is one of the main parameters used in quality control of gasoline and provides information about the resistance to auto ignition. This phenomenon occurs when the temperature of the fuel–air mixture under the effect of compression, leading to sufficiently increased self-detonation of the mixture without the help of a spark [2]. In order to improve the octane quality of a gasoline fraction, the refinery industry uses some high-octane rating components that are paraffinic in nature. The octane index is improved by increasing the degree of iso-alkane branching. For example, 2,2,3-trimethylbutane has a research octane number (RON) 112, whereas the RON of *n*-heptane is zero. Since these highly branched isomers have a relatively low environmental impact, the skeletal isomerization of *n*-alkane can be a key technology for production of high quality gasoline [3].

This process typically was carried out over bifunctional metal/acid catalysts and the catalysts that are often used for isomerization of linear-chain alkanes usually contain Platinum (Pt), which is supported on chlorinated alumina [4]. However, these catalysts cause corrosion and are very sensitive to poisons such as water, aromatics, and sulphur [5].Previous study reported that the platinum supported on Mordenite zeolite (Pt/H-MOR) has been used commercially for the isomerization of linear alkanes to higher octane branched isomers. This zeolite has strong acidity and is very suitable for small alkanes, giving a high yield of isomers. However, the practical application of this process has only been confined to C_4/C_6 alkanes, because the isomerization of long-chain alkanes is usually accompanied by undesirable cracking.

Thus, catalysts with a sufficiently good balance of metal and acid functions under suitable reaction conditions are generally needed to suppress cracking in order to achieve high isomerization selectivity for long-chain alkanes. Molybdenum oxide (MoO_3) supported catalysts have been extensively studied in recent years due to their possible potential to catalyze the isomerization of linear alkanes [6]. Matsuda and co-workers have reported that the hydrogen reduced of MoO_3 gave an active and selective isomerization catalyst, in which its activity was greatly influenced by its extent of reduction [7]. Besides, Ledox and co-workers showed that oxygen-modified Mo_2C and carbon- modified MoO_3 were active for heptane isomerization [8].

Based on previous study, catalyst support is one of the crucial factors that influence the catalyst acidity [9]. Therefore, in this study mesostructured silica nanoparticles (MSN) was used as the MoO_3 catalyst support and its activity towards *n*-heptane conversion was compared with others catalysts using HZSM-5 and MCM-41.

2.0 METHODOLOGY

2.1 Catalyst Preparation

MSN was synthesized by co-condensation and sol-gel methods according to the procedure in the literature [10]. The 5 wt. % MoO_3 supported catalysts were prepared by impregnation of MSN, HZSM-5 and MCM-4 with an aqueous solution of ammonium heptamolybdate solution (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$) followed by drying at 383 K and calcination in air at 823K.

2.2 Characterization of Catalyst

Fourier Transform Infra-Red (FTIR) measurements were carried out using Agilent Carry 640 FTIR Spectrometer. Before the analysis, catalysts were activated at 623 K for 1 h. In the pyridine adsorption process, the activated catalysts were exposed to 2 Torr of pyridine at 423 K for 15 min, followed by outgassing at 423 K and all spectra were recorded at room temperature [11].

2.3 Catalytic Testing

The isomerization of *n*-heptane was conducted in a microcatalytic pulse reactor at 623 K. Prior to the reaction, 0.3 g of catalyst was activated in an oxygen stream (F_{Oxygen} = 100 mL/min) at 623 K for 1 h, followed by hydrogen stream ($F_{Hydrogen}$ = 100 mL/min) at 623 K for 3 h. A dose of *n*-heptane (0.5μmol) was passed over the activated catalyst, and the products were trapped at 77 K before flash-evaporation into an online 6090 N Agilent Gas Chromatograph equipped with FID and HP-5 Capillary Column and an FID detector. The conversion of *n*-heptane ($X_{n\text{-heptane}}$) was calculated according to Eq. (1):

$$X_{n-heptane} = \frac{\sum A_i - \sum n-heptane}{\sum [A]_i} \qquad (1)$$

where, A_i is the corrected chromatographic area for particular compound.

3.0 RESULTS AND DISCUSSION

3.1 Structural Properties of Catalysts

The textural properties of all catalysts are listed in Table 1. The MoO_3-HZSM exhibited the lowest surface area compared to the MoO_3-MCM-41 and MoO_3-MSN. For the total pore volume, the MoO_3-MSN showed the highest value followed by MoO_3-MCM-41 and MoO_3-

HZSM-5. This is might be attributed from the presence of small interparticles and intraparticles inside the MSN support.

Table 1 Textural properties of catalysts

Catalysts	Surface area [m²/g]	Total pore volume [cm³/g]
MoO₃-HZSM-5	355	1.9
MoO₃-MSN	648	8.3
MoO₃-MCM-41	632	6.6

Nitrogen adsorption-desorption isotherm and corresponding pore size distribution of all catalysts are shown in Fig. 1. The MoO_3-HZSM-5 showed a type I profile characteristics of microporous material, accompanied by a small hysteresis loop at higher pressure, which reveals some intergranular mesoporosity [12]. The pore size distribution of MoO_3-HZSM-5 showed a narrow and monomodal pattern, with a peak pore width at 1.17nm (Fig. 1A). The MoO_3-MSN showed a type IV profile and type H1 hysteresis loops (Fig. 1B), corresponded to mesoporous materials with highly uniform cylindrical pores. In particular, the MoO_3-MSN exhibited two steps of capillary condensation with the first step at P/P_o = 0.25, indicating the presence of intraparticles mesopores inside the MSN support.

Figure 1 Nitrogen adsorption isotherms of and average pore width of (A) MoO₃-HZSM-5 (B) MoO₃-MSN (C) MoO₃-MCM-41obtained from NL-DFT method.

Secondly, a small hysteresis loop was observed at higher pressure P/P_o = 0.95, attributed to interparticle textural porosity, which indirectly reflects the size of particles. In previous study, it has been reported by Kim et al., that the capillary condensation at higher partial pressure was associated with a smaller particle size [13]. The pore size distribution of MoO_3-MSN showed a peak of pore width at 4.57 nm. The MoO_3-MCM-41 showed a type IV adsorption isotherms based on IUPAC classification. The catalyst exhibited almost similar isotherm to MoO_3-MSN with an adsorption step at relative pressure at P/P_o = 0.25 due to the capillary condensation of N_2 inside intraparticles pores. However, it should be noted that the MoO_3-MCM-41 had no interparticle pores at P/P_o

= 0.95. For the pore size distribution, the MoO_3-MCM-41 showed a peak of pore width at 4.57 nm.

3.2 Acidic Properties of Catalysts

FTIR spectroscopy using pyridine as probe molecule was employed to identify the types of acid sites by recognizing the absorbance band formed between the acidic sites and probe molecules. The FTIR pre-adsorb pyridine spectra on all catalysts are shown in Figure 2(A). The catalysts were activated at 673 K and the spectrum was recorded after the adsorption of pyridine on samples reach equilibrium at 423 K, and the physisorbed state was subsequently removed by heating at 573 K under vacuum. Thus, the resulting absorbance bands indicated only strong adsorptions between the pyridine molecules and acidic sites.
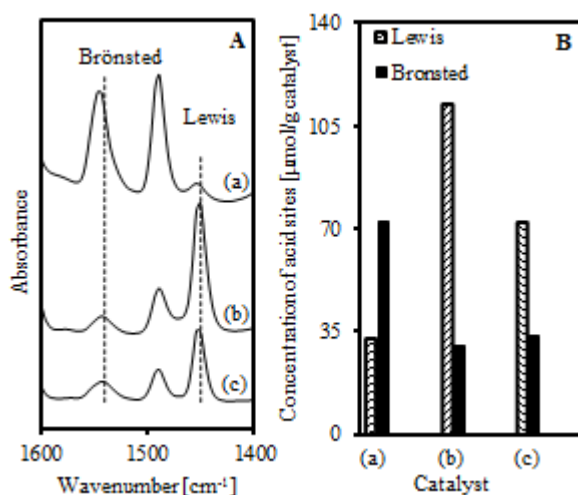

Figure 2: FTIR spectra of pyridine adsorbed on (a) MoO₃-HZSM-5, (b) MoO₃-MSN and (c) MoO₃-MCM-41, activated at 673 K, followed by pyridine adsorption at 423 K and outgassed at 423 K. (B) Gaussian deconvolution area of Brönsted and Lewis acid site of (a) MnoO₃-HZSM-5, (b) MoO₃-MSN and (c) MoO₃-MCM-41.

All of the catalysts showed an absorbance band at 1545 cm⁻¹ which correspond to C-N stretching of pyridinium ions ($C_5H_5NH^+$) bound to Brönsted acid sites on the catalysts surface, while the band at 1454 cm⁻¹ was correspond to the vibration of physically adsorbed pyridine bound to Lewis acid sites [14]. The concentration of pyridine on both acid sites was calculated according to the literature [15] and was illustrated in Figure 2(B). The concentration of pyridine on Lewis acid sites was in order of MoO₃-MSN > MoO₃-MCM-41 > MoO₃-HZSM-5, while the concentration of Brönsted acid was in order of MoO₃-HZSM-5> MoO₃-MCM-41 > MoO₃-MSN.

3.3 Isomerization of *n*-Heptane

The catalytic activities of the MoO_3 supported catalysts were tested for *n*-heptane isomerization at 623 K in a microcatalytic pulse reactor, by using

hydrogen as carrier gas. The conversion of *n*-heptane over all catalysts is shown in Table 2. The MoO$_3$-MSN exhibited the highest conversion of *n*-heptane of followed by MoO$_3$-MCM-41 and MoO$_3$-HZSM-5. Since the result obtained was in accordance with the concentration of Lewis acid sites from FTIR pre-adsorb pyridine, it is suggested that the high Lewis acid in the MoO$_3$-MSN may facilitate the formation of active protonic acid sites from molecular hydrogen through hydrogen spillover mechanism [16]. Previously, it has been reported that the formation of protonic acid occurred when dissociated hydrogen molecules go through a surface dissociation to Lewis acid site, followed by losing an electron to become a proton. The Lewis acid site that accepted an electron reacts with a second hydrogen atom to form a hydride connected to Lewis acid site. Thus, a pair of proton and hydride is produced from a hydrogen molecule on the catalyst surface [17].

Table 2 Conversion of *n*-heptane over MoO$_3$ supported catalysts at 623 K in the presence of hydrogen

Catalysts	Conversion [%]
MoO$_3$-HZSM-5	7.3
MoO$_3$-MSN	18.7
MoO$_3$-MCM-41	8.6

The previously produced protonic acid sites play important roles in the *n*-heptane isomerization since the formation of *n*-heptyl carbenium ion should be initialized by the interaction between the *n*-heptane and protonic acid [18]. Isomerization process proceeds by acid catalyzed reaction mechanism in which the isomerization was induced by the interaction between the *n*-heptane and protonic acid site to form *n*-heptyl carbenium ion. Next, the carbenium ion was isomerized to branched heptyl carbenium ion. The product of iso-heptane was produced by the interaction between branched heptyl carbenium ion and hydride ion followed by desorption form the surface of catalyst. Based on the result reported by Setiabudi et al, the presence of protonic acid site and hydride ion was significant in *n*-heptane isomerization, since the formation of iso-pentane products increased by the concentration of protonic acid sites [19].

Besides, the difference in catalytic activity of all catalysts could be attributed by the textural properties of the catalysts. The high conversion of *n*-heptane over MoO$_3$-MSN might be due to the presence of both inter and intra-particles in the MSN support, which led to high dispersion of MoO$_3$ metal on the catalyst surface. Thus, it was suggested that this property contributes to the easiness of the acid sites accessibility. In addition, the interparticle pores could facilitate the transport of the reactants and products molecules during the catalytic reaction, making MoO$_3$-MSN more accessible for n-heptane isomerization. This result was in agreement with previous report by Khitev et al. that proved that the presence of interparticle pores or intercrystalline ordered mesopores in FER zeolite has improved the skeletal isomerization of 1-butene [20].

The comparison of *n*-heptane conversion over other catalysts is presented in Table 3. Liu et. al. has reported that modification of MoO$_3$ with phosphate gave a conversion 6% of *n*-heptane. Meanwhile the supported metal with HMCM-22 and Hß support gave a conversion of 13.7 and 18 %, respectively [21]. Based on the results, it can be suggested that the activity of MoO3-MSN is comparable with other type of catalysts for n-heptane isomerization.

Table 3 Catalytic conversion of *n*-heptane isomerization over different catalysts at 623 K

Catalysts	Conversion [%]
Mo/P	6.0
MoP/HMCM22-40%	13.7
MoP/Hß-40 %	18.0
WP/Hß-40 %	15.2

4.0 CONCLUSION

Mesostructured silica nanoparticles (MSN) and a series of MoO$_3$ catalysts with different supports (HZSM-5 and MCM-41) were successfully prepared by a sol-gel and impregnation method for the isomerization of *n*-heptane. The conversion of *n*-heptane at 623 K reaction temperature followed the order of: MoO$_3$-MSN > MoO$_3$-MCM-41 > MoO$_3$-HZSM-5. This indicates that MoO$_3$-MSN possesses high potential as a support for n-heptane isomerization. The catalytic performance of the MoO$_3$-MSN was closely related to the acid property of catalyst. The presence of high concentration of Lewis acid in MoO$_3$-MSN facilitated the formation of protonic acid sites for the isomerization reaction. Besides, the presence of both inters and intra-particle porosity in the structure of MSN support has improved the catalytic performance compared to the other supported MoO$_3$ catalysts.

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