

Paper ID: A115

Isomerization of Linear C₅-C₇ over Pt Loaded on Protonated Fibrous Silica@Y Zeolite (Pt/Hsi@Y)

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EXTENDED ABSTRACT

Silica-based fibrous material has been extensively studied by researchers after the discovery of fibrous silica nanosphere (KCC-1) by Polshettiwar *et al.*, 2010. The KCC-1 was first prepared using the microwave-assisted hydrothermal technique exhibited excellent properties, including a high surface area, a fibrous surface morphology, good thermal and hydrothermal stabilities and mechanical stability. Moon, *et al.*, (2012) reported that the mesoporous silica with fibrous morphology has high surface area compared with a typical hexagonal or cubic pore structure which suitable for good catalytic support. Previous study has many discovered related to the acid-catalyzed for isomerization reaction. They discovered that the isomerization supports must have appropriated acidity for the good catalytic activity. However, the KCC-1 which fully composed with silica does not provided an adequate acid sites to promote acid-catalyzed isomerization reaction [1,2]. In the present work, newly combined zeolite-based with fibrous silica was prepared via self-assembly process in the microemulsion system. This new catalyst has a potential to overcome inadequate acidity provided by KCC-1. Therefore, implementation of combined silica based material with zeolite enhanced the acidity of the catalyst to overcome the inadequate acidity provided by solely silica of KCC-1. The high acidity will enhanced the isomerization reaction towards producing high octane number gasoline [3].

Fibrous silica Y zeolite (Si@Y) was prepared using Y seed (Zeolys, CBV 901, Si/Al: 80) crystal-seed crystallization. HSi@Y and Pt/HSi@Y were prepared according to the method described in previous report [4]. In brief, Pt/HSi@Y was prepared by incipient wetness impregnation of HSi@Y with H₂PtCl₆·6H₂O in aqueous solution to obtain 0.5 wt% Pt in the finished catalyst. The mixture was then stirred and placed in oven until dried and calcined at 823 K for 3 hours. For comparison study, the method was repeated for HY and Pt/HY. The sample was labelled as Pt/HY and Pt/HSi@Y.

The crystallinity of catalysts was determined by using XRD analysis. The XRD patterns of HY, HSi@Y, Pt/HY, and Pt/HSi@Y attributed to the Faujasite-type structure of zeolite Y (JCPDS card 77-1549) for all catalysts at diffraction peaks of 2θ = 3–40°. The typical peaks of the catalysts are well matched with commercial HY suggested that the catalysts have the zeolite Y characteristics which can be observed at 6.3°, 10.3°, 12.2°, 15.9°, 20.8°, and 24.0° [5]. The introduction of fibrous silica in HY zeolite decreased the crystallinity of HY to about 24 %. However, the addition of Pt on HY and HSi@Y did

not significantly change the crystallinity of the catalysts. Fig. 1 shows the FESEM image of spherical fibrous morphology and particle size distribution of Pt/HSi@Y. The Pt/HSi@Y exhibited bicontinuous lamellar grow radially outward from the zeolite core which arranged in three dimensions to form a colloidal sphere shape with open pore channels [1]. This unique fibrous silica morphology mimics the KCC-1 proposed by Polshettiwar, *et al.*, (2010). The KCC-1 was suggested have several advantages such as high surface area for high accessibility of the bulky mass reactant to active sites and thus increases the rate of reaction and product formation. The particle size distribution of HSi@Y is in the range of 500-700 nm. Upon the introduction of Pt, there were no significant changes in morphology and particle size of HSi@Y. The EDX analysis revealed that the catalysts were composed of Si, Al, and O atoms. The addition of Si species from hydrolysis of TEOS by urea resulted in an increase amount of Si on Pt/HSi@Y catalyst from 85.5 to 94.0 wt%. This can be claimed that Pt/HSi@Y possessed dendrimeric silica fibers which arranged in three dimensions to form a sphere. This result is supported by a Si/Al ratio obtained with MPAES and EDX analysis, in which HSi@Y type catalysts possessed higher Si/Al ratio as compared to commercial HY. The Si/Al ratio of HSi@Y increased from 42 to 108, while the addition of Pt did not change the Si/Al ratio of HSi@Y. According to XRD, NMR and FESEM results, it can be showed that Pt/HSi@Y was predominantly composed of silica and small part of the Y zeolite framework. The center of Pt/HSi@Y was consist of Y zeolite and on the outer part (dendrimer) was mainly composed of silica. This phenomenon was mimic with the previous report where the elemental mapping showed the aluminosilicate framework of ZSM-5 was on the center of Pt/HFZSM-5 sphere and the silica was mainly distributed at the outer part of the Pt/HFZSM-5 sphere [4,7].

N₂ physisorption of HSi@Y exhibited type IV isotherms with H₃ hysteresis indicated the presence of mesopores with the high BET surface area and pore volume. HSi@Y exhibited slightly higher surface area (550 m²/g) as compared to HY (473 m²/g). The total pore volume of HSi@Y is 0.808 cm³/g in which it showed that HSi@Y possessed more mesopores and micropores volumes than HY (0.308 cm³/g). The increase in a BET surface area of HSi@Y type catalysts may be due to the formation of dendrimeric silica upon the silica addition to the parent HY. The increased in the amount of mesopores from 0.044 to 0.710 cm³/g was suggested due to the formation of dendrimeric silica which suggested that the porosity formed between the dendrimeric silica was revealed as mesopores.

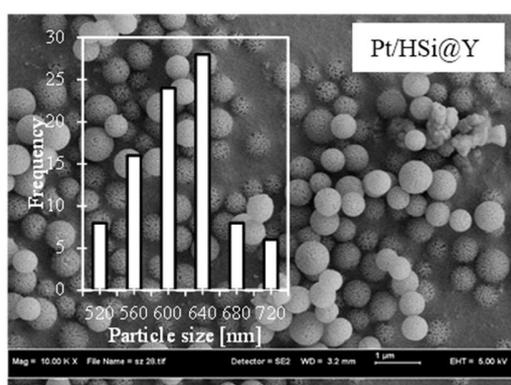


Fig. 1 FESEM images and particle size distribution of Pt/HSi@Y.

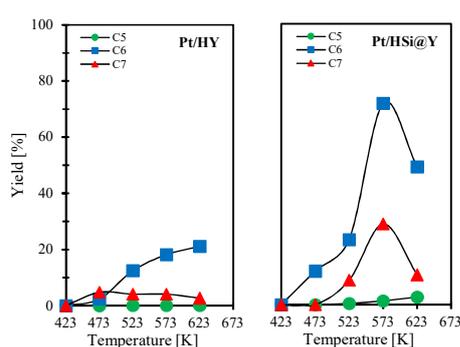


Fig. 2 Yield isomer products for isomerization of *n*-pentane, *n*-hexane and *n*-heptane at different reaction temperatures over Pt/HY and Pt/HSi@Y

The catalytic activities of HY, HSi@Y, Pt/HY and Pt/HSi@Y catalysts were evaluated with respect to C₅, C₆ and C₇ isomerization at 573 K in a microcatalytic pulse reactor in the presence of hydrogen gas. Fig. 2 shows the yield of isomer product for the isomerization of C₅, C₆ and C₇ over Pt/HY and Pt/HSi@Y. The results showed that Pt/HSi@Y has better catalytic activity on C₆ and C₇ isomerization than C₅. Pt/HSi@Y exhibited high activity and it increased continuously with reaction temperature up to 573 K. However, at 573 K above, the yield drastically decreased due to thermal cracking process. In contrast, only C₆ isomerization yielded product under this reaction condition. Based on this results, it can be suggested that the presence of silica fiber in the outermost shell of HY enhanced the catalytic activity of Pt/HY. Generation of protonic acid sites from hydrogen molecules was observed in all catalysts which was observed by pyridine preadsorbed IR spectroscopy in the presence of hydrogen gas. The abundance of Lewis acid sites in the Pt/HSi@Y generated more protonic acid sites in the presence of hydrogen. From these results, it was concluded that Pt/HSi@Y was the versatile catalyst for generating abundance of protonic acid sites due to the presence of more Lewis acid sites from dendrimeric silica fibers.

Keywords: Pt/HSi@Y; Fibrous Silica; Y zeolite; acidic sites; C₅-C₇ isomerization

Acknowledgment

This work was supported by the Ministry of Higher Education Malaysia through Fundamental Research Grant Scheme no. 4F781 (FRGS/1/2015/SG06/UTM/01/10).

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