Fibrous silica encapsulated mordenite zeolite (HMOR@KCC-1) was prepared by using microemulsion system coupled with zeolite crystal-seed crystallization technique. While the activity of the catalysts were tested for n-hexane isomerization in a microcatalytic pulse reactor. XRD analysis shows reduction of modernite crystallinity phase due to silica encapsulation. IR studies of pyridine adsorption gave the concentration of both Brönsted acid sites (BAS) and Lewis acid sites (LAS). 2,6-Lutidine as probe molecule showed that Pt/HMOR contains strong Brönsted acid sites while Pt/HMOR@KCC-1 contains medium strength Brönsted acid sites. The relatively mild acid sites and improved acid sites accessibility introduced by the fibrous silica morphology enhanced the catalytic yield of Pt/HMOR@KCC-1 by 22% compared to Pt/HMOR in isomerization of n-hexane.

Generally, isomerization of n-alkanes is done over a bifunctional catalyst consisting of metal sites for hydrogenation/dehydrogenation and acid sites for the skeletal isomerization. Typical examples of isomerization catalysts are platinum supported on various zeolites [1]. Zeolites are very versatile support materials that can be tailored to accomplish optimum performance in a wide range of applications [2]. In recent years, extensive research on zeolites has been devoted to a detailed description of the active sites in the zeolite structure. The application of Pt/HMOR has received considerable attention in isomerization of n-hexane. Several reports indicated that zeolites suffer low molecular diffusion efficiency, quick catalyst deactivation and consequently, weak activity to bulky molecules [3]. In order to overcome these limitations, development of catalysts with both mesoporosity and appropriate acidic properties have being the subject of exploration. Improving the catalytic performance is a vital issue for enhancing the efficiency and yield of the process [4].

Herein, infrared spectroscopy of pyridine and lutidine with different size and basicity were used to study the strength and accessibility of acid sites in Pt/HMOR@KCC-1 and its application in n-hexane isomerization.

Fibrous silica encapsulated mordenite zeolite was prepared by microemulsion system coupled with zeolite seed assisted crystallization according to previously reported procedure [2]. Typically, the microemulsion system consist of water–toluene–1-butanol in which tetraethyl orthosilicate (silica source) was assembled on the surface of mordenite particles with the assistance of cetyltrimethammonium bromide (surfactant) and urea. The crystalline structure of the catalysts were determined with X-ray diffraction (XRD) recorded on powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Kα radiation source in the range of 2θ = 5–40°. Fourier Transform Infrared (FTIR) measurements were carried out using Perkin–Elmer Spectrum GX FT-IR Spectrometer. The acidity of the catalysts were investigated by adsorption of pyridine and lutidine.
probe molecules at 150 °C and room temperature for 15 min respectively. The samples were further outgassed at several temperatures (50-200°C). The isomerization of \( n \)-hexane was conducted in a microcatalytic pulse reactor at temperature of 150-350 °C.

The XRD patterns of all studied catalysts are illustrated in Figure 1A. The observed peaks are the characteristic diffraction peaks reported for mordenite [5]. The decrease in relative crystallinity in the present study is likely as the result from the formation of fibrous silica. As shown in the inset FESEM figure, the HMOR@KCC-1 consist of spherical particles with diameter ranging from 100-180 nm and well crystallized surfaces. The IR spectra of the pyridine adsorbed on all studied catalysts activated at 400°C are shown in Figure 1B. Two bands at 1545 and 1454 cm\(^{-1}\) are ascribed to pyridinium ions adsorbed on BAS and pyridine adsorbed on LAS respectively. The abundant LAS on fibrous mordenite based catalysts as indicated by the intense band at 1454 cm\(^{-1}\) may be due to the unsaturated cations on the exposed surface as well as the Si-OH electron pair acceptor of the silica fibers [6]. However, the parent mordenite zeolite catalysts exhibited higher number of BAS from bridging hydroxyl groups (SiOHAl).

Figure 1: (A) XRD pattern and (B) IR spectra of pyridine adsorbed for all catalysts

Figure 2A and 2B shows the absorbance bands at 1640 cm\(^{-1}\) and 1465 cm\(^{-1}\) ascribed to lutidine adsorbed on BAS and LAS respectively. Pt/HMOR showed no significant change in the intensity of bands of adsorbed lutidine for both BAS and LAS even after desorption at high temperatures. This indicates that the catalyst contains strong BAS and LAS. However, Pt/HMOR@KCC-1 showed remarkable decrease in the band intensity of BAS at high temperature which indicate the presence of medium/weak BAS and LAS. Pt/HMOR@KCC-1 gave the highest isomer yield of 74% with 76% conversion and 94% isomer selectivity (Figure 2C). This further confirmed the improved active sites accessibility introduced by the fibrous morphology which enhanced the catalytic performance of Pt/HMOR@KCC-1.
Figure 2: FT-IR spectra of 2,6-lutidine (a) adsorbed onto (A) Pt/HMOR, (B) Pt/HMOR@KCC-1 outgassed at (b)room temperature, (c)50, (d)75, (e)100, (f)125, (g)150, (h)175 and (i)200 °C and (C) Catalytic performance of all catalysts in n-hexane isomerization at 350°C.

Keywords: Fibrous silica KCC-1; Mordenite; Acidity; Platinum; n-hexane; Isomerization.

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