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Hydroconversion of *n*-hexane over Pt-supported on fibrous silica mordenite catalysts: effect of transition metals on acidity and activity

M Ibrahim^{1,4}, A A Jalil^{1,2*}, W F W Zakaria¹, M Izan³, A A Fauzi¹ and I Hussain³

¹School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

²Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

³Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

⁴Department of Chemical Engineering, Abubakar Tafawa Balewa University, PMB 0248, Bauchi, Bauchi State Nigeria

*aishahaj@utm.my

Abstract. The effect of incorporation of either Zr, Co, Mo or Zn on Pt/HFSM was investigated for the hydroconversion of *n*-hexane in a pulsed micro-reactor at a temperature range 423-623 K. The acidity of all the studied catalysts were investigated using pyridine adsorption and Fourier Transform Infrared Spectroscopy. The FTIR-pyridine study showed that the catalysts possessed different concentration and strength of both Lewis and Brønsted acid sites. It was revealed that the moderate acid sites distribution on PtZr/HFSM and PtZn/HFSM facilitated the isomerization of the intermediate hexene while the strong acid sites were selective towards cracking reaction. The trend for the bimetallic catalysts studied in *n*-hexane hydroisomerization is in the order: PtZr/HFSM>PtZn/HFSM>PtMo/HFSM>PtCo/HFSM. The highest activity for hydrocracking and hydrogenolysis were exhibited by PtMo/HFSM and PtCo/HFSM respectively. The PtZr/HFSM exhibited the highest hydroisomerization activity due to the moderate acidity and abundant Lewis acid sites capable of generating protonic acid sites by the hydrogen-spill over phenomena.

1. Introduction.

Generally, hydroconversion of *n*-alkanes is done over a bifunctional catalyst consisting of metal function and acid sites for the rearrangement of the intermediate species [1]. Typical example of such catalysts are platinum supported on zeolites. Zeolites are widely utilized support materials that can be modified to accomplish optimum efficiency in a various applications [2]. In recent years, extensive research on zeolites has been devoted to a detailed description of the active site in the zeolite structure. Several reports indicated that zeolites suffer low molecular diffusion efficiency, quick catalyst deactivation and consequently, weak activity. The application of Pt/HMOR has received considerable attention in hydroconversion of *n*-hexane, several strategies for modification of the properties of modernite were reported with both improved mesoporosity and appropriate acidic properties. Improving the catalytic performance is a vital issue for enhancing the selectivity of the process [3].



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Herein, infrared spectroscopy of pyridine was used to study the acid sites concentration and strength in metal promoted Pt supported fibrous silica mordenite catalysts, prepared by microemulsion system assisted seed-recrystallization. The synthesized catalysts were loaded with Pt and second metals as promoters and tested in the hydroconversion of *n*-hexane.

2. Experimental

2.1 Preparation of parent fibrous silica mordenite

Fibrous silica mordenite (FSM) was synthesized using a microemulsion system via self-assembly process. Briefly, *n*-butanol and toluene were mixed, tetraethyl orthosilicate (TEOS) was added to the mixture and stirred vigorously in a Teflon. Subsequently, a solution prepared from CTAB, urea, and water as the template, mordenite as seed was quickly added into the mixture. After vigorous stirring to obtain homogeneity in the solution, the mixture was exposed to 4 h hydrothermal treatment at 393 K. The solid products were centrifuged, washed with deionized water and dried in oven for 24 h at 383 K. Finally, the synthesized material was calcined at 823 K for 6 h. The H-form was obtained by ion exchange with ammonium nitrate solution and calcined at 823K denoted as HFSM.

2.2 Preparation of metal loaded HFSM

The metal precursors were used to load 5 wt% of each on to HFSM support via the incipient wetness impregnation technique. The respective precursors are zirconium ($\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$), cobalt ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), molybdenum (MoO_3) and zinc ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). The solid catalysts obtained were dried overnight in an oven at 383 K and calcined at 823 K for 3 h. All the synthesized catalysts were loaded with 0.5 wt% platinum with an aqueous solution of chloroplatinic acid (H_2PtCl_6) as Pt precursor denoted as PtCo/HFSM, PtZn/HFSM, PtZr/HFSM and PtMo/HFSM.

2.3 Characterization

The XRD pattern were obtained with Bruker Advance D8, 40 kV, 40 mA recorded using Cu α radiation of 0.15418 nm at a 2θ angle ranging from 5° to 40° with scanning rate of 0.02° . The morphological structure of the catalyst was examined using FESEM-EDX JEOL JSM-6701F. Pyridine was used as adsorbed probe molecule to study the acidity of the catalyst. Pressure of 2 Torr was established for the adsorption of pyridine at 423 K for 30 mins. The strength of the Brønsted acid sites and Lewis acid sites were analysed by pyridine desorption at Low (423 K), medium (523 K) and high (623 K) temperatures for 30 mins.

2.4 Catalytic testing

The catalytic performance of synthesized catalysts was tested for *n*-hexane hydroconversion in a micro-catalytic pulse reactor at 423-623 K and ambient pressure under hydrogen stream. Briefly, 0.2 g of catalyst was pretreated with flowing oxygen stream for 1 h and hydrogen stream for another 3 h, both at a flowrate of 100 ml/min and 673 K, it was subsequently cooled down to 423 K in the hydrogen stream. The temperature was allowed to stabilize, then 2 μmol dose of *n*-hexane was passed over the activated catalyst. The reactor effluent was trapped at 77 K, followed by flash-evaporation and the products were analyzed by an online 6090N Agilent Gas Chromatograph equipped with an HP- 5 Capillary Column and an FID detector. The selectivity (*Si*) of particular product were calculated according to Equations 1.

$$Si(\%) = \frac{[C]_i}{\sum [C]_i - [C]_{\text{residual } n\text{-hexane}}} \times 100 \quad (1)$$

Where the molar concentration are represented by $[C]_i$ for a particular product and $[C]_{\text{residual } n\text{-hexane}}$ for residual *n*-hexane.

3. Results and discussion

3.1 Synthesis mechanism

The formation mechanism for fibrous silica mordenite zeolite (FSM) is illustrated in figure 1. Firstly, a typical synthesis involves the formation of microemulsion system consisting of water-toluene-1-butanol by using CTAB as template and urea [4]. Mordenite seed act as primer, the hydrophilic interaction of the CTAB head with the mordenite zeolite forming reverse micelles while the organic phase interacts with the hydrophobic tail. The most important step in the resultant mesoporous structure being the microspheres formed from CTAB template, the negatively-charged surface of mordenite served as the nucleation center. Butanol facilitates the CTAB incorporation on mordenite zeolite at the initial stage while urea which act as a catalyst, provides the basic condition for the hydrolysis of TEOS with TEOS as the precursor [5]. Furthermore, this well oriented arrangement of the CTAB formed a template for hydrolyzed silica growth on the mordenite. Finally, the silanol groups and ethanol obtained as hydrolysis proceed condense to form repeated unit of Si-O-Si (polysiloxane) by cross-linking process. Then, the calcination process removes all the organic matter and surfactants in the template ultimately giving rise to the core-shell structured FSM with radially oriented fibrous silica on the mordenite core.

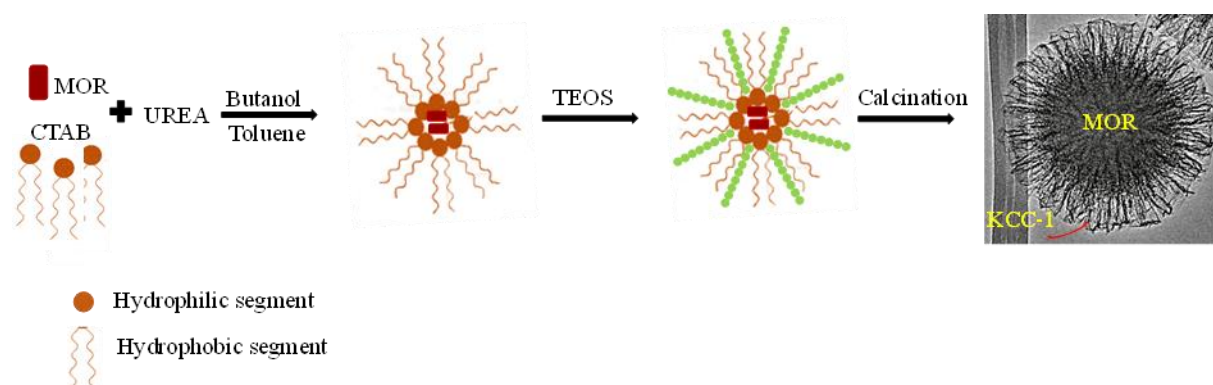


Figure 1. Schematic illustration of the formation process of fibrous silica mordenite (FSM).

3.2 Morphology and crystallinity study

The surface study carried out by field emission scanning electron microscopy (FESEM) revealed that the FSM consist of microspheres with diameter in the range of 650-750 nm with fibrous morphology as depicted in figure 2. The crystalline structure of FSM as determined by XRD analysis is presented. The diffraction peaks at $2\theta = 6.55^\circ, 8.85^\circ, 9.76^\circ, 13.52^\circ, 15.40^\circ, 19.70^\circ, 22.42^\circ, 25.73^\circ, 26.44^\circ$ and 27.64° corresponds to the characteristics peaks for mordenite zeolite as identified by JCPDS data card no. 43-0171[6]. These results confirmed the incorporation of fibrous silica onto mordenite.

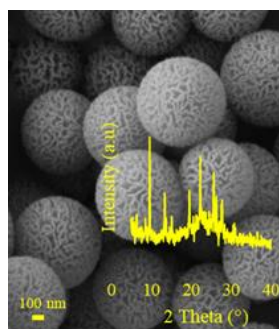


Figure 2. FESEM image and XRD pattern of fibrous silica mordenite.

3.3 Acidity study

The type and strength of acid sites have a strong influence on the catalytic performance in *n*-hexane hydroconversion. In order to investigate acidic properties of the studied catalysts, pyridine as probe molecule was adsorbed on the samples. The IR spectra of pyridine adsorbed on metal promoted Pt supported protonated FSM (HFSM) catalysts and then desorbed at different temperatures are shown in figure 3. The adsorption band at 1545 cm^{-1} corresponds to pyridinium ions adsorbed on Brønsted acid sites while the adsorption band at 1454 cm^{-1} corresponds to coordinately adsorbed pyridine on Lewis acid sites [7]. It is well known that the framework of mordenite consist of silica (SiO_4) and alumina (AlO_4) tetrahedrally connected. The bridging OH (Si-OH-Al) correspond to the Brønsted acid sites. Besides, the aluminum species not in the zeolite framework described as extra-frame work aluminum (EFAI) as well as the metal modification account for the Lewis acid sites. As shown in figure 3, the acid strength is determined after desorption of pyridine at 423 K, 523 K and 623 K and the amount of pyridine on the catalyst corresponds to weak, medium and strong acid sites respectively. PtZr/HFSM has the highest amount of Lewis acid sites. Both PtZr/HFSM and PtZn/HFSM displayed a moderate acidity as both catalysts retained about 50% of the pyridine after desorption at 623 K. It is obvious that PtCo/HFSM has the highest amount of Brønsted acid sites and new acidic centers for Lewis acid sites. In addition, it loses small amount of the adsorbed pyridine even at high reaction temperature of 623 K. This is an indication of high concentration of strong acid sites possessed by the catalyst. The PtMo/HFSM also retained about 75% of the adsorbed pyridine at 623 K.

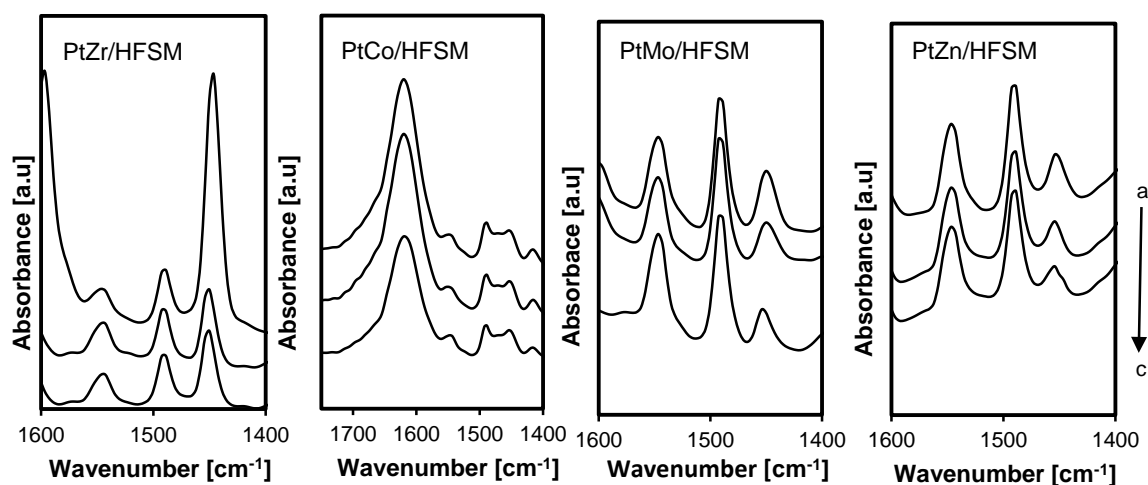


Figure 3. FT-IR spectra of pyridine desorbed at (a) 423 K (b) 523 K and (c) 623 K.

3.4 Catalytic performance

The catalytic activities of bimetallic catalysts promoted with different promoters as a function of reaction temperatures in terms of rate of conversion and selectivity are presented in figure 4 and figure 5 respectively. The activity in *n*-hexane hydroconversion is in the following order: PtMo > PtZr > PtZn > PtCo. The significant increase in activity for all catalysts was observed with reaction temperature (figure 4). The rate of conversion for PtMo/HFSM was higher by a factor of 10 at 623 K for *n*-hexane hydroconversion.

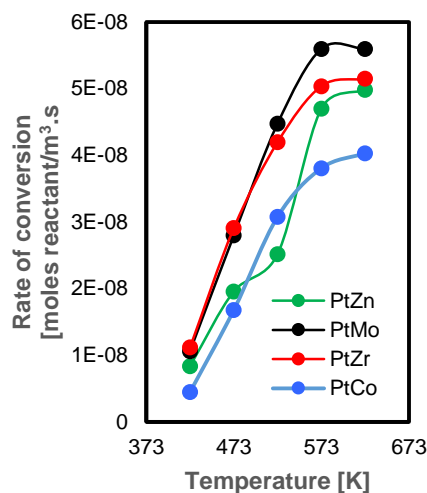


Figure 4. Catalytic performance of all studied catalysts.

For hydroisomerization, the selectivity is in the following order: PtZr > PtZn > PtMo > PtCo for *n*-hexane at all the temperature range investigated. The moderate acidity especially in Lewis acid sites for the PtZr/HFSM catalyst favors hydroisomerization. For hydrocracking activity, the following order was observed PtMo > PtCo > PtZn > PtZr. Meanwhile, for hydrogenolysis, PtCo/HFSM showed the highest selectivity probably due to the strong and abundant Brønsted acid sites (figure 5).

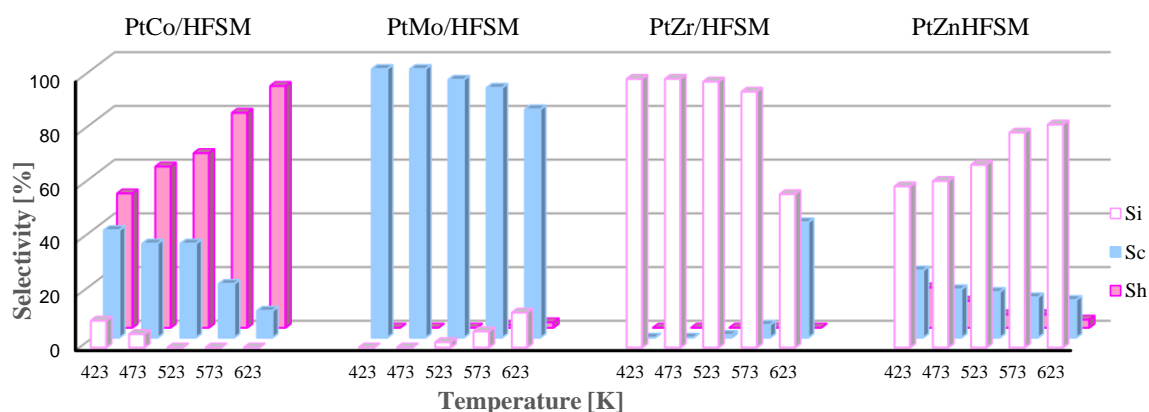
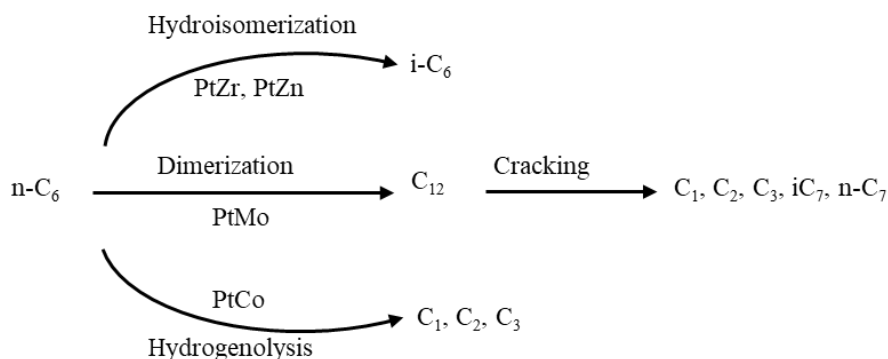


Figure 5. Product selectivity for hydroconversion of *n*-hexane (Si-hydroisomerization selectivity, Sc-cracking selectivity and Sh-hydrogenolysis selectivity).

Scheme 1. depicts the plausible mechanisms of *n*-hexane hydroconversion over metal promoted Pt-HFSM catalysts with different metals. All catalysts were active in the hydroconversion, hydroisomerization proceeds over Zr and Zn promoted catalysts while the cracking reaction was predominate over Mo promoted catalyst. Hydroisomerization process involves the bifunctional mechanism by which the Pt dehydrogenate the *n*-hexane and that is subsequently rearranged by acid catalyzed reaction in which the isohexene were formed [8]. The presence of medium strength acid sites and abundant Lewis acidity was significant in *n*-hexane isomerization, hence the increase in formation of iso-hexane products as the intermediates easily desorbed from the acid sites. The hydroisomerization products (iso-hexane) were generated by the hydrogenation of the iso-hexene intermediates. For the Mo promoted catalyst, cracking reaction proceeds via a dimerization-cracking pathway as observed in the product distribution. The hydroconversion process involves the dimerization of *n*-C6 to form *n*-C12 and subsequent formation of higher hydrocarbons and cracked

products. However, for Co-promoted catalyst, the hydrogenolysis of *n*-hexane overwhelmed the reaction chemistry, as the absence of higher hydrocarbon products exclude the possible dimerization-cracking pathway [7]. Most likely, hydrogenolysis occurs on the surface of PtCo/HFSM catalyst with very strong acid sites enabling longer residence time to create the environment for such process to occur.



Scheme 1. Plausible reaction mechanisms for *n*-hexane hydroconversion over PtM/HFSM catalysts with different metals (Zr, Zn, Mo and Co).

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