SYNTHESIS AND CHARACTERISATION OF A NOVEL MESOPOROUS ZSM-5 ZEOLITE CATALYST FOR THE CONVERSION OF BIOETHANOL TO AROMATICS AND C_5+ HYDROCARBONS

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1.0   Introduction

Zeolites are unique aluminosilicate materials known for their crystalline and microporous structures [1, 2]. These properties make them highly versatile and suitable for various applications, including catalysis, adsorption, and water filtration [3-5]. In particular, zeolites have found significant use as solid acid catalysts in the oil refining and petrochemical industries due to their exceptional attributes, such as high activity, strong acidity, shape selectivity, thermal stability, and cation exchange capacity [6-8]. The successful commercialisation of zeolite catalysts has driven advancements in hydrothermal synthesis technologies, leading to a wide range of microporous and macroporous materials with diverse topologies and morphologies [9]. The hydrothermal synthesis of zeolites involves subjecting reaction media containing ionic solutions to supercritical or near-supercritical temperatures within sealed containers, resulting in unique microporous structures and altered physical and chemical properties of the media [9]. However, this process typically requires specific temperature, pressure, and reaction time conditions, leading to high energy consumption [9-12]. To enhance the catalytic performance of ZSM-5 catalysts, researchers have introduced metal species into the zeolite framework to modify and increase the selectivity of aromatics and liquid fuel hydrocarbons in the low alcohol to hydrocarbon (LATH) reaction [13-19]. Incorporating metals into the ZSM-5 framework has been found to improve catalytic activity by altering acidity and texture [20-22]. For example, incorporating nickel in ZSM-5 catalysts improved acid strength and hydrothermal stability, reducing coking and dealumination while converting ethanol to petrol (ETG) [21]. Metals play crucial roles in dehydrogenating alkanes, producing olefin, which undergoes protonation and subsequent isomerisation, cracking, and reversal phases [23]. Studies involving iron-doped ZSM-5 zeolites and mesoporous Zn/ZSM-5 zeolite demonstrated increased catalyst life and improved yield of liquid hydrocarbons [24]. Similarly, nano-H [Zn, Al] ZSM-5 showed remarkable selectivity for liquid hydrocarbons and excellent catalytic stability Ni, et al. [25].

Despite their remarkable attributes, zeolites have limitations due to their small pore size, restricting the catalysis of reactions involving large molecules. To address this, researchers have sought to produce zeolites with meso- and macroporous pore configurations, which offer superior catalytic efficacy compared to regular zeolites. In light of this, the current research aims to develop a novel ZSM-5 zeolite catalyst with enhanced mesoporous structures and modify it with a transition metal to enhance its catalytic performance in converting ethanol to hydrocarbons. Furthermore, the study analyses the impact of various operational factors on the ethanol-to-hydrocarbon transformation process.

2.0   Method

To synthesise the mesoporous ZSM-5 support catalysts, the hydrothermal technique was employed, involving the mixture of an appropriate amount of TPABr as the organic structure-directing agent, along with aluminium sulfate and water glass as sources of aluminium and silica, respectively. Concurrently, the dry impregnation approach was adopted to introduce iron species, ensuring successful incorporation without affecting the catalyst framework or the crystalline phase of the standard ZSM-5. The resultant catalysts were named 0.5Fe and 5Fe, denoting 0.5 and 5 wt%Fe doping, respectively. Various characterisation methods were employed to analyse the newly synthesised catalyst, including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Fourier transform infrared (FT-IR), and nitrogen adsorption. The performance of pure and metal-modified catalysts was investigated in converting ethanol to hydrocarbons at temperatures of 350 and 400 °C and weight hourly space velocities (WHSV) of 5 and 12 h^{-1}. To assess the outcome of the catalytic process, a gas chromatograph (GC) model YL6500 was employed, allowing for the analysis of both gaseous and liquid hydrocarbons produced during the catalytic reaction.

3.0   Results and Discussion

3.1   Catalyst Characterisation Results

Various characterisation techniques were employed to gain a comprehensive understanding of the synthesised catalysts. Crystal structure analysis was carried out using a Bunker D2 Phase X-ray diffractometer (XRD) to examine the undoped ZSM-5 and iron-doped ZSM-5. The XRD results confirmed that the catalysts maintained the characteristic crystalline phase of standard ZSM-5 even after iron doping, as evidenced by distinct peaks at specific angles (Fig. 1a). Functional group analysis was performed using a Perkin Elmer Fourier Transform-Attenuated Total Reflectance-Infrared Spectrometer (Spectrum-2) to identify the chemical interactions within the zeolite framework. The study revealed that the Ni-doped catalysts retained the characteristic functional groups of HZSM-5, providing evidence of vital chemical interactions inside the zeolite framework (Fig. 1b). Microscopic examination was conducted using a ZEISS Sigma 300 VP microscope with scanning electron microscopy (SEM) to investigate the intrinsic morphology of the samples. High-magnification images showed the formation of microspheres through the aggregation of nanosized crystals, revealing the unique structural features of the catalyst (Fig. 2). Importantly, the addition of Fe species did not alter the overall morphology of the zeolite, ensuring the preservation of its catalytic function.

Surface area and porous features were determined using an N$_2$ adsorption-desorption analyser, providing insights into the zeolites' porosity and surface characteristics. Mesopores were observed in the zeolite structure, and the introduction of metal species appeared to influence the pore structure. With the incorporation of Fe, a reduction in surface area, total pore volume, and mesopore volume was observed, especially at higher metal loading (5 wt%). This reduction could be attributed to the accumulation of metals, leading to the blocking of zeolite channels' surfaces by Fe species (Fig. 3). The comprehensive characterisation data revealed that both the unaltered and Fe-doped HZSM-5 catalysts exhibited essential features for converting bioethanol into aromatics and hydrocarbons. The presence of mesopores and the preservation of crucial structural and functional attributes indicate the catalyst's potential to support effective catalytic reactions during the ethanol-to-hydrocarbon (ETH) conversion process. Overall, these findings highlight the suitability of the as-synthesised HZSM-5 and Fe-doped HZSM-5 catalysts for bioethanol conversion and further, emphasise their promise as

efficient catalysts for this important transformation process. The combination of various characterisation methods has provided valuable insights into the catalysts' properties, paving the way for their potential application in sustainable biofuel production.
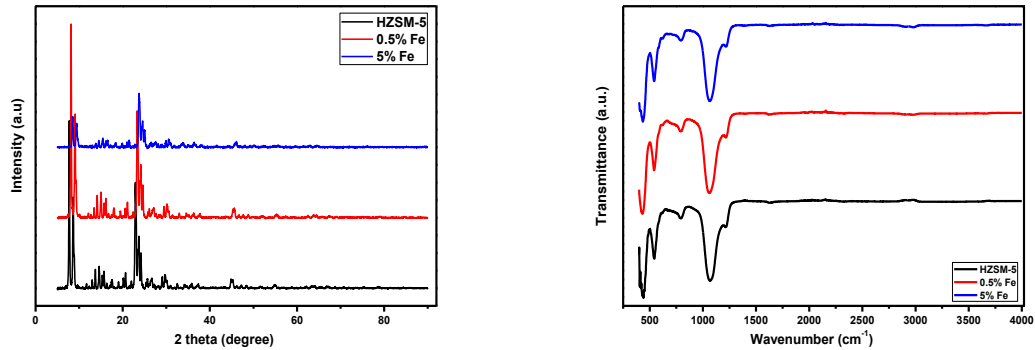

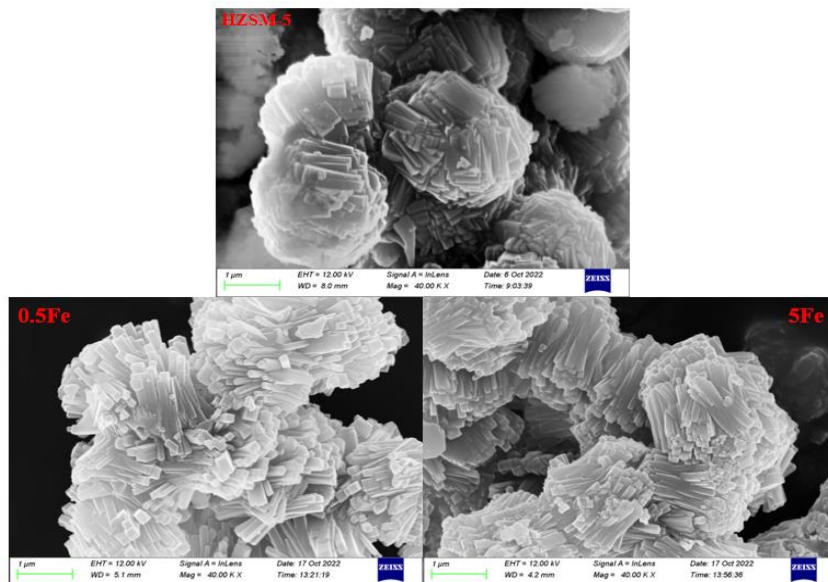Figure 1. XRD (a) and FTIR (b) spectra of unmodified and Fe-doped catalysts

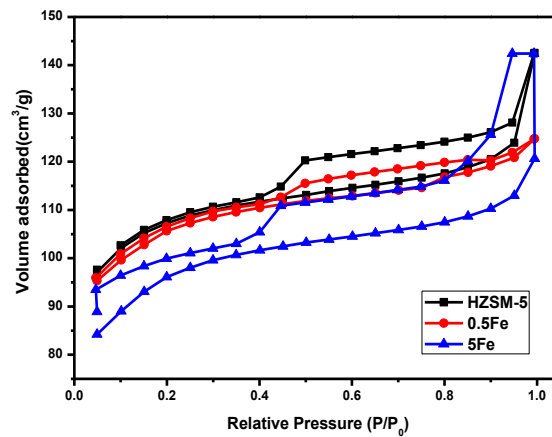Figure 2. SEM images of unmodified and Fe-doped HZSM-5 catalysts

Figure 3. N_2 adsorption/desorption isotherms of synthesised catalysts

3.2   Catalytic Performance

At all process stages, the unmodified and Fe-doped catalysts exhibited ethanol conversion rates of >98%. The distribution of products tended toward gaseous products, with the unmodified catalyst exhibiting the highest selectivity (85.2%) for C_1-C_4 hydrocarbons compared to the Fe-doped catalysts at 5 h^{-1} and 350 ^{o}C. However, at 5 h^{-1} and T=400 ^{o}C, the Fe-doped catalysts with 0.5% and 5% Fe showed decreased selectivity for BTX and C_5+ hydrocarbons (as shown in Fig. 5c and d). It is noteworthy that liquid hydrocarbon yield (LHY) was low at this WHSV, with 0.5Fe-doped catalyst recording the highest BTX (10%) and C_5+ (42.3 %) hydrocarbon (Fig. 4a). As the residence time decreased, the selectivity for gaseous C_1-C_4 hydrocarbons decreased, promoting the formation of C_5+ hydrocarbons. This shift was attributed to an increase in WHSV to 12 h^{-1}, which promoted the production of liquid hydrocarbons, including C_5+ (Fig. 4b). Compared to the previous WHSV, the WHSV of 12 h^{-1} improved BTX and C_5+ synthesis as Fe-doped catalysts recorded the highest selectivity at both temperatures investigated. This observation is in agreement with the study by [26]. This increase in LHY was attributed to the secondary oligomerisation reaction, which promoted the synthesis of liquid hydrocarbons [27]. This trend was observed for all catalysts studied. Interestingly, despite the change in operating conditions, the temperature did not show significant variations for C_5+ yield at 12 h^{-1}. Compared to temperature changes, the change in WHSV resulted in significant changes in the product distribution, which can be attributed series of secondary reactions, including catalyst deactivation due to coke deposition [28]. These factors influence the overall performance of the catalysts during the ethanol conversion process. It can be deduced that the Fe-doped catalysts exhibited excellent ethanol conversion rates throughout the process, with product selectivity favouring gaseous and liquid hydrocarbons under certain operating conditions. Understanding these different properties and the effects of various parameters on product distribution is critical to optimising the catalytic process and improving the production of valuable liquid hydrocarbons. In addition, mitigating deactivation effects is critical to achieving long-term stability and efficiency in biofuel production. According to the proposition by Schulz and Bandermann [29], higher temperatures during the reaction can lead to the integration of gaseous products such as ethylene or diethyl ether into an ethanol molecule that is chemisorbed on the catalyst's surface. This phenomenon can lead to longer aliphatic chains, some of which can rapidly transform into aromatic compounds depending on the reaction conditions. Our study supports that ethylene and diethyl ether are likely the primary gaseous products resulting from ethanol conversion at temperatures below 350 degrees Celsius and low WHSV (Weight Hourly Space Velocity). Conversely, more reactions are expected to yield liquid hydrocarbon molecules as the temperature increases.

In summary, higher temperatures during the ethanol conversion reaction can influence the formation of gaseous products like ethylene and diethyl ether, which may subsequently interact with ethanol molecules adsorbed on the catalyst's surface. This process can lead to the formation of longer aliphatic chains, with the potential for rapid transformation into aromatic compounds depending on the specific reaction conditions. Our findings support the idea that ethylene and diethyl ether are the main gaseous products at lower temperatures and low WHSV while increasing the temperature is likely to promote the synthesis of liquid hydrocarbons.
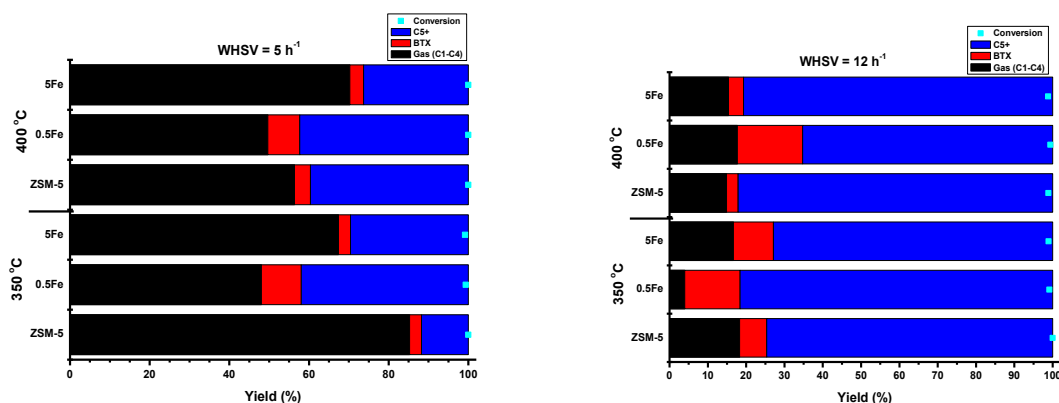
Figure 4. Product distribution at WHSV of 5 h^{-1} (a) and 12 h^{-1} (b) operating conditions for ETH conversion

4.0 Conclusion

Mesoporous ZSM-5 zeolites were hydrothermally synthesised and doped with Fe species. Optimised operating conditions employed during the synthesis process resulted in improved mesoporous HZSM-5, while the incorporation of Fe species into the zeolite framework was effectively achieved by dry impregnation. Characterisation techniques provided valuable insights into the properties of the synthesised catalysts, revealing characteristic peaks and functional groups associated with a typical MFI zeolite framework. Catalyst evaluation demonstrated that incorporating Fe species improved the catalytic performance and product selectivity. Varying operating conditions affected the product distribution as WHSV of 12 h^{-1} favoured liquid product yield, including aromatics (BTX) and C$_5$+ selectivity. This study demonstrates the effect of WHSV and temperature on product distribution and selectivity during ethanol conversion with HZSM-5 zeolite catalysts. Understanding these temperature-dependent effects is critical for optimising the catalytic process and developing efficient and selective strategies for biofuel production. By fine-tuning the Fe loading and optimising reaction conditions, the catalytic performance of Fe-doped catalysts can be further enhanced to achieve higher selectivity towards desired liquid products, which is crucial for successfully implementing bioethanol as a sustainable petrochemicals and fuel source. The successful synthesis and catalytic performance showed that these catalyst holds promise in bioethanol conversion and application as a viable alternative fuel and underscore the significance of catalyst development in advancing the renewable energy and green chemistry field. Future research in this direction is expected to unlock even greater potential in biofuel production and accelerate the transition towards a more sustainable energy landscape.

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