

# *Review Article*

# **Overview of Current and Future Perspectives of Saudi Arabian Natural Clinoptilolite Zeolite: A Case Review**

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After a thorough review of existing studies of clinoptilolite zeolites, three areas for potential investigation of the Saudi Arabian zeolites were found. They are the characterizations, the catalytic activity, active sites, and uses of natural clinoptilolite zeolites. First, no analysis is available worldwide to compare the percentage weight of local zeolites with those sourced from other countries, nor does one exist for the establishment on the zeolite conversion of MBOH with water on acidic catalysts at lower temperatures. Secondly, a review of current literature on the topic revealed that basic and active sites of Saudi Arabian zeolites have yet to be examined. Future investigation of zeolite catalytic activity can be achieved by methyl butynol test reaction (MBOH) and absorption-desorption of ammonia. In the characterization of a range of international materials, the methyl butynol test reaction was utilized, including on natural zeolites, natural clays, and synthesized hydrotalcites. However, the catalytic performance of natural Saudi Arabian clinoptilolite zeolites by test reaction of MBOH conversion has not been yet investigated. Therefore, this article also includes an outline of the general testing conditions and parameters required to execute the accurate characterization of local Saudi clinoptilolite under optimal test conditions. Likewise, knowledge of the important active acidic centers of local materials is prescribed. This can be ascertained by determining the conditions together with the test parameters for the application of the "temperature-programmed desorption of ammonia" method in order to obtain an accurate determination of local Saudi clinoptilolite acidic centers. Additionally, an outline of the catalytic activity of worldwide clinoptilolite is given in this article together with kinetic investigations of other sources for the clinoptilolite zeolite in order to form the basis for the testing of local Saudi clinoptilolite. The percentage average of chemical composition (Wt.%) of natural clinoptilolite from various countries is also included. Finally, a future research plan is proposed here. This will form the basis for a complete study or survey to be compiled detailing the modifications needed to increase the surface areas for Saudi natural clinoptilolite zeolites using different methods of modifications. This could enhance its application as acid catalysts for use in the retardation of coke formation and for membrane separation on cationic exchange.

## 1. Introduction

In general, zeolites are of great interest to researchers working in the various fields such as energy recovery technology [1], water adsorption [2], ion exchangers, adsorbents, catalysts [3, 4], acid-catalyzed dehydration of alcohols [5–7] for dry reforming of methane [8], and synthesis of zeolites with nonporous titania for corrosion resistance applications [9], as well for agriculture and food production [10].

There are a number of definitions; though not dissimilar, the most widely accepted is by Breck [11]. Depending on the size of the pore opening, the aluminosilicates are divided into narrow, medium, and wide-pore zeolites. The narrow pore zeolites have a pore opening consisting of eightmembered rings, each of which corresponds to a diameter of 0.4-0.5 nm. The medium pore zeolites have pores with a diameter of 0.5-0.6 nm, which are composed of tenmembered rings, and the wide-pore ones are bounded by pore openings with ten-membered rings, each of which equals a diameter of 0.70–0.75 nm [4]. With a production of about 1,000,000 t/a, the ion exchangers produce the largest amount in the zeolite industry [12]. For example, the synthetically produced zeolite NaA is used as a substitute for sodium polyphosphate in laundry detergents.

Since zeolite NaA is the preferred substitute for calcium and magnesium ions; it has proven to be an adequate substitute [13, 14]. In the technical application of zeolites as selective adsorbents [15], the processes are divided into two application fields. On the one hand, zeolites are used as drying agents in insulating glass panes and coolant circuits. On the other, the advantage of Zeolites as a hugely important technical application is in their capacity for dynamic adsorption in the treatment of natural gas (removal of water), the separation of isomeric hydrocarbons, and the enrichment of oxygen from air [4, 13, 16].

Due to zeolites' well-defined pore structure and their acidity, scientific and industrial interest in them is very high. The main fields of application are ion exchange in detergents, adsorption for the separation and purification of substances, and as catalysts zeolites, which are mainly used, in the petrochemical industry [17, 18]. Examples of typical application are for catalytic cracking (FCC), hydrocracking, and the MTG process (methanol-to-gasoline) [4, 13, 15, 17].

Additionally, coke formation is another challenge for refinery industry. Since this challenge exists, investigation on local material is beneficial. Suggested characterizations, when are applied, would also provide information about active centers and how they might be modified precisely, including data on their selective adsorption capability. Two methods, namely, the catalytic test reaction of methyl butynol (MBOH) and the temperature program desorption of ammonia method are suggested in this paper as an effective characterization tools to abstract more information about catalytic activity and active acidic centers of the local zeolite. Note that both suggested methods have yet to be implemented on the local Saudi zeolite in particular. Hence, the conditions and parameters for both methods are summarized in the current paper. Results from both analysis will be reported and contribute to the field of knowledge. From this point, the paper presents literature review on that case and then proposes a research approach for the local Saudi zeolite where the conversion of MBOH with water can be applied for local zeolites as acidic catalyst using conversion of MBOH with water at lower reaction temperature of 120°C.

Though there is an ample amount of published works in the general field of zeolites, much less is available related to local natural Saudi Arabian zeolite. Hence, this work, focuses on local sources and discusses its significance and potential use in a variety of industrial applications. In the general published works, samples and examples of reaction provide the bases on which investigation into local clinoptilolite zeolite may be further developed, synthesized, and modified in order to produce an increase in efficiency and reduction in costs. Different factors impact the development of the zeolite material in between: the ratio of silica to alumina and the level of impurities determined by geographical source. Attention is also given in this review to comparing the close similarities of the chemical composition of local clinoptilolite zeolite with that given in the general literature and its modification, also considering geographical sources internationally.

*1.1. Zeolite ZSM-5.* The zeolite ZSM-5 is a synthetic 10-ring zeolite and the formula for describing the composition is [16]

$$\operatorname{Na}_{n}\left[\operatorname{Al}_{n}\operatorname{Si}_{96-n}\operatorname{O}_{192}\right] \cdot 16\left(\operatorname{H}_{2}\operatorname{O}\right) \tag{1}$$

The ZSM-5 belongs to the group of pentasils, which can reach a Si/Al ratio of 10 to infinity. The high silicon content results in high thermal stability, hydrophobicity, and strength, but it leads to fewer active sites [18–20]. In the literature [16, 21], description of two types of channels of the ZSM-5 is found. First, there are the linearly extending channels along the internal structure [010] with a pore openings of 0.53 nm  $\times$  0.56 nm whereas the second has sinusoidal channels with a pore openings of 0.51 nm  $\times$  0.55 nm along the same. The framework of Beta zeolite is made up of three closely related polymorphs. They consist of similar layers, which follow each other in varying order. Two of these polymorphs form a pair of enantiomers. The layers result in a three-dimensional pore structure consisting of three interconnected 12-ring channels [19].

*1.2. Zeolite-Y.* The zeolite-Y belongs to the group of faujasites whose unit cell represents the following formula [19]:

$$Na_{58}[Al_{58}Si_{134}O_{384}] \cdot 240(H_2O)$$
 (2)

The connection of cuboctahedra as a tertiary unit via sixmembered rings leads to the three-dimensional structure of the Y zeolite. The arrangement of the polyhedra leads to the formation of large cavities, which are called super cages due to their diameter of 1.2 nm [19].

### 2. Natural Clinoptilolite: Catalytic Activity

Clinoptilolite is closely associated with the series of zeolite tectonic-silicate minerals named Heulandite (HEU). The structural makeup of HEU is a framework of tetrahedral SiO<sub>4</sub> and AlO<sub>4</sub> units and is formed by the intersection of three sets of channels, A, B, and C. The first two, A and B, run parallel to the *c* axis. Channels A comprise tightly compressed rings of ten members with an aperture of  $3.1 \times 7.6$  Å [20]. The B channels have an eight-membered aperture width of  $3.6 \times 4.6$  Å. Conversely, the C channels parallel the *a*-axis. Likewise, they are limited to eight-ringed apertures of  $2.6 \times 4.6$  (Å). The clinoptilolite unit cells system are monoclinic with a C2/m [20, 22–25] space group. The general chemical formula which represents clinoptilolite is (Na,K)<sub>6</sub>Al6Si<sub>30</sub>O<sub>72</sub> · 20H<sub>2</sub>O [26, 27] with a varying Si/Al ratio of 4.0 to 5.3.

Furthermore, natural clinoptilolite from China (Jiutai, Jili) [23] with a molecular formula  $Na_8[Al_8Si_{40}O_{96}]32H_2O$  was investigated. This natural clinoptilolite exhibits an oblique crystal form and with a channel size (Å):  $4.0 \times 5.5$ ,  $4.4 \times 7.2$ ,  $4.1 \times 4.7$ , a volume of 34 (%), and a density of 1.74 (g/cm<sup>3</sup>) [23]. The catalytic activity of natural clinoptilolite

from Cuba (Castilla) [28] was also investigated, capitalizing on the advantages of using the o-xylene isomerization. The results reveal a significantly low activity due to possible countercations of the samples that subsequently limit the accessibility of substrate to the natural zeolite channels [28].

However, treating natural clinoptilolite with acids improved and increased the channel openings [29]. Another example presented in the literature [30] cited a natural clinoptilolite from a deposit in Slovakia (Kucin) [30]. These natural samples were investigated for the liquid isomerization of  $\alpha$ -pinene. After treatment with HCL, bicyclic products were produced. The conversion of  $\alpha$ -pinene reached to around 40% after approximately three hours of the reaction time while products' selectivities ranged from 30 to 58%. In addition, the  $\alpha$ -pinene initial reaction rate ( $r_o$ ) was estimated at 120°C with value of 8.7 mmol-pinene/g<sub>cat</sub> min [30].

Additionally, the catalytic activity over clinoptilolite was examined utilizing the advantageous methanol to dimethyl ether [31, 32], and a high catalytic activity was shown [32]. Furthermore, a preparation of ZSM-5 catalysts from natural clinoptilolite was successfully achieved [33]. The new synthesized zeolite sample was then examined for benzene conversion and found to exhibit a similar conversion to ZSM-5 zeolite of the referenced sample [33, 34]. On other hand, the results of transmission electron microscopy for silver nanoparticles on natural clinoptilolite deposited from Mexico (Oaxaca) [35] revealed a homogeneous distribution and the sorption kinetic investigations and exhibited good matching between various adsorption theoretical models. Higher correlation factors for silver nanoparticles on natural clinoptilolite in relation to the experimental values were recorded [35]. The highest correlation values for the firstorder Lagergren model were given in the concentrations of 3 and  $4 \text{ mg} \cdot L^{-1}$  [36].

In addition, synthesized palladium nanoparticles on natural clinoptilolite was achieved [37]. The high-resolution transmission electron microscopy (HRTEM) image of  $Pd^0$ nanoparticles showed reticular lattice planes inside the nanoparticles with crystal structure of clinoptilolite [37]. The synthesized sample was then investigated by Ullmann condensation and Sonogashira coupling reactions and alkynes. Results presented high yields under mild reaction conditions in water [36].

To date, no Saudi Arabian zeolite deriving from any type of natural clinoptilolite has reportedly been synthesized. Further investigations to clarify this matter are paramount. In addition to the insight into catalytic activity reactions of local natural and sourced clinoptilolite presented in Section 2, Section 3 details the various research methods and approaches adopted for investigating the different types of zeolite. Given that comparatively little work has been conducted so far on the local Saudi clinoptilolite resource, a new database, based on past and current studies, should be created in order to investigate them further.

More recently, research [38] has shown that decationation of mordenite clinoptilolite led to a slight decrease in the water adsorption capacity. At the same time, a decrease in adsorption capacity of water was observed during the process of dealumination [38]. 2.1. Zeolite Catalyzed Dehydration. The dehydration reaction using zeolites has long been well understood [38–44] and it can be carried out in acidic as well as alkaline media. However, preference is given to acid catalysts in the literature [45–49].

The reaction is both highly dependent on the conditions as well as the constitution of the alcohol used. Increased temperatures are usually required for the acid-catalyzed reaction. Furthermore, the ease of dehydration increases with increasing degree of substitution of the hydroxylbearing carbon atom. Primary alcohols are difficult to assess for dehydration. In general, the readiness of water elimination increases in the order of primary, secondary, and tertiary alcohol [45]. There are three possible methods of elimination reactions methods, which are outlined below. When the reaction is acid-catalyzed, the hydroxy group of the alcohol acts as a proton acceptor, resulting in the formation of alkyl oxonium ions (Figure 1).

In the alkyl oxonium ion, the carbon-oxygen bond is weakened compared to that of the alcohol. In Figure 2, it can be seen that the bond is subsequently split heterolytically to form alkyl-carbenium ion and water. This elimination pathway is called the E1 mechanism, and dissociation can be considered as a rate-determining step. The dissociation is followed by the cleavage of a proton to form an olefin [47].

Disassociation is a reversible reaction because the water as a Lewis base can recombine with the carbenium ion, which is a Lewis acid. The tendency to form the carbenium ion increases from primary to tertiary alcohol. The reason for stabilizing the ion is its chemical environment. Alkyl groups have a greater positive inductive effect compared to hydrogen atoms, which have a stabilizing effect on the carbenium ion. Furthermore, it leads to hyper conjugation. This can be regarded as a kind of electron thrust of an alkyl substituent in the direction of an electron-deficient center [47]. The dehydration of alcohols may lead to the formation of unwanted by-products. The reaction has different orientations as soon as an alcohol is used which carries one or more alkyl groups in the vicinity of the carbenium ion catalyzed by acid; the hydroxy group of the alcohol is deprotonated. The resulting ion can be stabilized by rearrangement reactions in order to produce a larger product splitting [47]. In addition to rearrangement, reactions occur when using nucleophilic acids such as hydrobromic acid and hydrobromic acid to substitution reactions that compete with the elimination. After proteolysis, the anionic halide acts as a nucleophile, which can substitute for the oxonium ion formed (Figure 3). In the group of halogens, the anions of iodine and hydrobromic acid are the main substitutes because they have a sufficiently high nucleophilicity compared to chloride ions. Targeted production of haloalkanes requires an excess of acid [47, 49].

In Figure 4, it can be seen that the use of nonnucleophilic acids such as sulfuric or phosphoric acid may result in the formation of ethers as by-products. After protonation of the alcohol, a protonated alcohol may attack as a stronger nucleophile at elevated temperatures. In this case, the formation of an ether occurs with dehydration [50, 51].



FIGURE 1: Formation of an alkyl oxonium ion [45].



FIGURE 2: Heterolytic cleavage of the alkyl oxonium ion followed by olefin formation [46, 47].



FIGURE 3: Substitution as a competitive reaction [47].



FIGURE 4: Ether formation as a competing reaction to olefin formation [50, 51].

Catalytic dehydration of hexylene glycol (HG) results in the formation of 2-methylpenta-1,3-dienes (1,3-dienes) and its isomer 2-methylpenta-2,4-dienes (2,4-dienes). 4-Methylpent-4-en-2-ol (pentenol) is formed as an intermediate in this reaction. Figure 5 shows the reaction equation of this dehydration.

For industrial purposes, the 1,3-diene can be used in Diels-Alder reactions. It acts as a diene that undergoes a [4+2] cycloaddition with a dienophile. The product is a substituted cyclohexane derivative which has gained great importance, for example, in the production of fragrance compositions [52]. The dehydration is carried out on an industrial scale with hydriodic acid (57%). Since HG is a polyhydric branched alcohol, in addition to the formation of 1,3-diene, the formation of 2,4-diene as a by-product occurs [5]. Moreover, the formation of dimethyl ether from the switch grass gasification method was followed by steam reforming as given in the literature [53-57]. In his patent, Springer [53] describes the continuous as well as the discontinuous processes of dehydration of HG. In these processes, an acidic compound which acts as a catalyst is first dissolved in a glycol or glycol ether. The reaction was



FIGURE 5: Reaction of HG dehydration under catalytic influence [52].

performed at atmospheric pressure and at temperatures of between 90°C and 200°C. Mineral acids or organic acids such as sulfuric, phosphoric, or p-toluenesulfonic acid and salts thereof are suitable for use as an acidic catalyst. Diethylene glycol or propylene glycol was employed as glycols and diethylene glycol monobutyl ether; diethylene glycol dibutyl ether or tetra ethylene glycol monomethyl ether can be applied as the glycol ether. In this case, the glycols or the ethers were used as heat carriers. The desired product 1,3diene, is a conjugated diene meaning it is a system with alternating double and single bonds. As compared to nonconjugated dienes, delocalization causes stabilization of the compound, as given in the literature [47], and with respect to a terminal alkene (about 125 kJ/mol), compounds with two noninteracting double bonds can be expected to have twice as high hydrogenation heat (about 250 kJ/mol). The difference in hydrogenation heat between the conjugated and the isolated diene is about 15 kJ/mol. By exactly this amount, the conjugated diene is more stable than a system with no interacting double bonds [47].

2.2. Catalysts with Brønsted Acid Sites Such as Alumina and H-ZSM-5. Heterogeneously catalyzed dehydration reactions have been known since the end of the eighteenth century. The initial attempts [58] to understand the elementary processes of these elimination reactions were at the beginning of the twentieth century [58]. Alumina proved to be the first solid catalyst in this field [47, 59]. Over time, many studies [59-61] have been undertaken that have specialized in the conversion of alcohols to heterogeneous catalyst systems. In this case, metal oxides such as Al<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub>, SiO<sub>2</sub>, and WO<sub>3</sub>, as well as zeolites and sulfides such as MoS<sub>2</sub> or WS<sub>2</sub> in a temperature range of 100°C to 500°C were used. However, low temperatures (150°C to 240°C) favor the formation of ethers. Depending on the oxide, different selectivities were observed with respect to the product. Since dehydration and dehydrogenation are in competition, the product variety could be demonstrated using the example of the reaction of 2 propanol. The exact relationship between selectivity and property of the catalyst is not fully understood. However, it is believed that various catalyst sites are involved [60-62]. According to Pines and Pillai [62], the dehydration of alcohols is only possible if basic centers also occur in the vicinity of acidic ones. In this case, acidic Brønsted centers are able to protonate hydroxy groups of the alcohol. The basic center in turn receives a proton of alcohol. On the other hand, solid catalysts with Brønsted acid sites such as H-ZSM-5 were investigated for the dehydration of ethanol. The results showed that at low temperatures (150 to 200°C), diethyl ether was predominantly formed and at slightly elevated temperatures (around 250°C) led to the formation of ethane [63-68]. Other technologies were also considered for the formation of ethane [69]. By contrast, even higher temperatures lead to secondary reaction, which as a consequence have undesirable by-products such as aromatics or paraffins. In addition to the temperature affects, the Si/Al ratio was observed in terms of the product spectrum. It was found that the yield of ethene increases with decreasing Si/Al ratio while the formation of by-products also decreases. The dehydration reactions do not require high acid center densities. This conclusion regarding the Si/ Al ratio is corroborated by the fact that zeolites rich in silicon are capable of converting ethanol into ethene. It is believed that in addition to strong Brønsted acid sites, the hydrogen atoms of the silanol groups also show some dehydration activity [70-73].

# 3. Challenges and Future Perspective on Saudi Clinoptilolite Zeolite: Its Properties, Potential, Implementation, and Characterization Techniques

3.1. Overview of Saudi Arabian Natural Clinoptilolite Zeolite and Its Properties in Relation to Other International Sources. Review of the literature on the natural clinoptilolite zeolites [74, 75] has determined that natural zeolite can be sourced at 'Harrat Shama' in South Jeddah, Saudi Arabia for example. The Saudi Arabian natural zeolite has crystalline structure with irregular particle size shapes ranging between 50 and 200 nm. The natural Saudi clinoptilolite was investigated by EDX, and the average results from different five sites at "Harrat Shama" showed weight percentages in the presence of O, Na, Al, Si, S, K, and, Fe, with values around of 36.33 (Wt.%), 9.85 (Wt.%), 8.76 (Wt.%), 33.43 (Wt.%) 0.68 (Wt.%), 3.75 (Wt.%) and 7.22 (Wt.%), respectively [74, 75]. The surface areas of natural Saudi zeolite range approximately between 3.2 and 8.9  $m^2/g$  [74]. The notably low values of the surface areas determined are likely due to the blockage of the micropores (almost total). The results then, relate to only external surface values. Other studies [30, 35, 37] reported the value of specific surface areas revealed to be in the range of  $16 \text{ m}^2/\text{g}$  to  $60 \text{ m}^2/\text{g}$  [30, 35, 37]. Therefore, more investigations on the surface area for the Saudi Arabian natural clinoptilolite zeolites are essential in order to determine the nature of the blockages in the micropores or to discover if they are caused by other external factors. If it is found that surface area activity is attributed to micropore blockages, then other modification methods [29, 30] including nano form should be investigated.

In addition, clinoptilolite zeolites have framework (cagelike) interconnected channel structures with ability to exchange M Cations for various cations from solution [76, 77]. The parallel channels of clinoptilolite vary and own different numbered rings. The first channel (A) which contains 10member rings has size (Å): A,  $4.4 \times 7.2$ . The second channel has a size (Å)  $4.1 \times 4.7$  with eight member rings. Both A and B Channels are linked together with a third channel (C) which exhibits eight member rings. Channel C has a size (Å)  $4.0 \times 5.5$  [78–80]. The cation size exchange is accessible for small hydrated cations like K<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> [78] Moreover, clinoptilolite zeolites obtained from the Mineralogical Society of America (MSA) show high capacity for cation exchange (CEC =  $2.16 \text{ meq} \cdot \text{g}^{-1}$ ). In general, the cation selectivity for clinoptilolite has the following order [78–80]:

$$Cs^{+1} > Rb^{+1} > K^{+1} > NH^{+4} > Ba^{+2} > SR^{+2} > Na^{+1} > Ca^{+2}$$
  
> Fe^{+2,+3} > Al^{+3} > Mg^{+2} > Li^{+1}  
(3)

The US clinoptilolite has  $3.9 \times 5.4$  (Å) channel dimension and relatively high thermal stability. The formula used to represent the unit cell of the US clinoptilolite is (Na<sub>3</sub>K<sub>3</sub>) (Al6Si<sub>30</sub>O<sub>72</sub>) · 24H<sub>2</sub>O [35].

3.2. Potential and Proposed Implementation of Characterization Techniques and Methods. Table 1 presents the chemical composition of natural local clinoptilolite collected from various countries like Mexico, Japan, Greece, and Ukraine. In general, the ratio between silica to alumina [81–85] is an essential factor for the synthesis, crystallinity, and for the kinetics of the crystallization process of zeolites. Hence, the challenge still exists to conduct further investigations so as to estimate best parameters and conditions for their crystallization. This could be assigned as a future target in the investigation of local clinoptilolite zeolites with the goal of exploring its commercial utilization.

Recently, local studies in Saudi Arabia, on the natural material were carried out with the aim of determining its potential use in energy producing applications [74, 75]. The percentage chemical compositions for the local clinoptilolite zeolites is relatively close to that of other international sources [35, 38, 76–78, 81–84]. However, highest ratio of silica to alumina was found in countries like Japan [81] and Serbia [82]. In sample from the Ukraine, additional elements like  $P_2O_5$ , S, and  $CO_2$  were present in the local natural clinoptilolite [38].

On low cost, simple zeolite-based solution for the treatment of wastewater from an olive mill, M cations, and water molecules was examined on the US clinoptilolite zeolites [76–78]. Another example is the study of pyrolysis reaction performed recently [75], by using mesoporous MCM-41 followed by microporous ZSM-5 [86]. The two-stage catalytic pyrolysis of waste plastics endeavored to achieve a high content of gasoline range hydrocarbons in the product oil [75].

In general, zeolite materials show excellent application in fine chemical industries because of their advantage in hydrocarbon conversions [35]. Clinoptilolite Saudi zeolite from "*Harrat Shama*" in Jeddah was also investigated with the objective of improving the quality of liquid oil and the

Components	Chemical composition of natural clinoptilolite from different countries (wt.%)							
	Japan [81]	Serbia [82]	Greece [83]	China [84]	KSA [74]	Ukraine [38]	Mexico [78]	
SiO <sub>2</sub>	77.96	72.20	68.25	66.45	65.40	64.95	62.36	
$Al_2O_3$	14.02	12.20	13.19	13.30	11.60	12.23	13.14	
Fe <sub>2</sub> O <sub>3</sub>	1.30	5.70	1.41	1.49	1.88	1.06	1.63	
TiO <sub>2</sub>	—	0.90	0.17	0.19	0.15	0.20	0.39	
MgO	0.46	1.0	1.14	0.92	1.75	1.21	0.92	
CaO	1.23	5.0	0.75	3.97	3.30	3.22	2.72	
Na <sub>2</sub> O	1.15	0.50	4.12	1.02	1.50	0.70	3.99	
K <sub>2</sub> O	3.88	2.50	1.66	1.54	0.98	2.35	1.20	
FeO						0.22		
$P_2O_5$						0.11		
S						0.03		
$CO_2$						1.03		
H <sub>2</sub> O						12.33		

TABLE 1: Average of chemical composition (wt.%) of natural clinoptilolite from various countries.

noncatalytic pyrolysis of tire waste [74–76]. In relation to the modification of natural Saudi zeolite, researchers studied the local zeolite obtained from "*Harrat Shama*" [74, 75].

The result of depositing natural local zeolite with nonporous titania resulted in a novel biomimetic coat material. The new modified zeolite is fabricated to produce a potential anticorrosion application. Other forms of zeolite modifications are presented in the literature through modification of Y zeolites with TiO<sub>2</sub> fine particles and intercalating with Ag, which resulted in high performance of photocatalysts [75]. The applications of photocatalysis can be utilized in pollutants degradation [79].

Similar investigative procedures might also be employed with local Saudi Zeolite. Recently, local researchers from King Saud University [74, 75] utilized natural zeolite that consists of a major layer of mordenite and minor layer of clinoptilolite. The natural zeolite was milled to nano form size ranging between 20 and 160 nm. However, it was observed that effect of milling causes a reduction in the minor phase of clinoptilolite structure for natural zeolite. Hence, a recrystallization process using hydrothermal basic silicate solution was applied which showed a difference in increment area of about  $0.32 \text{ cm}^2/\text{g}$  from the original surface area. Moreover, factors that affect the crystallization process at the time of recrystallization and at the time of milling together with silica and OH- concentration have been studied [75].

The fact of the existence of impurities in natural zeolites composition still presents a challenge and has wide implementation for the continuing use of zeolites material employed in industrial applications. Additional investigations focused on designing hierarchical zeolites for petroleum refinery [87-91]. The importance of hierarchical zeolites results from their active acidic sites, which lead to high catalytic activity in the desired reaction [38, 83, 84]. A more detailed understanding of the characterizations and basic properties of modified local Saudi Arabian zeolite is important in order to assist in achieving the most optimum results in any future modification that may eventually be applied to a variety of industrial applications such as the catalytic condensation of glycerol using acetone. Hence, a variety of characterization techniques were described in the literature [92-99] used to characterize solid materials and to understand their behaviour

as well as to show their active acidic sites and basic properties. However, in order to ascertain the properties of local Saudi zeolite, the principle characterization methods and techniques methods employed are limited to only X-ray diffraction, scanning electron microscopy, UV-Vis spectroscopy, and X-ray fluorescence (XRF) [74, 75]. The absence of a wider variety of characterization methods results in the lack of specific data in understanding catalytic activity and acidicbasic properties during reaction of the local Saudi zeolite materials. More specific data may be acquired by the implementation of the characterization methods such as methyl butynol (MBOH) test reaction [95]. Table 2 details the test conditions and parameters required for the successful optimization of MBOH test reaction. Additionally, the literature reports other techniques which include both a method for estimating basic active sites, namely, the temperatureprogrammed desorption of carbon dioxide and, for the characterization of the acidic sites, the temperature-programmed desorption of ammonia [92-99]. The overriding advantage of employing the proposed techniques is that the result will lead to a fuller understanding of zeolite catalytic activity during reaction. Specifically, exploration and the accrued knowledge of dehydration catalytic reaction at specific temperatures will later serve to inform on zeolite acidic or basic active sites during reaction. A review of the advantages and the practical implementations of employing such characterization techniques using the various kinds of zeolites is given in the literature [21, 92–100]. Moreover, it is possible to retard coke formation [101] by utilizing local eight-ring clinoptilolite zeolite as acid catalyst. The conversion of MBOH with water on an acidic catalyst or by incorporation of local nanosize zeolites as an example with platinum and palladium may also be established at a lower temperature so as to capture carbon oxysulfide (COS). Summary of conditions and parameters for characterizations of different natural materials in between zeolites using catalytic test reaction of methyl butynol (MBOH) [99, 102] is detailed in Table 2 [95]. Future investigations in this direction would contribute in adding more information about the local material catalytic limit performance as well to offer to the local industry, a potential catalyst support with a low cost for CO oxidation from industrial off gases and with an adequate temperature. The

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Conditions	Parameters
<ul><li>(1) Activation procedure</li><li>1.1. Oxidation in air: Heating rate: 1 h to 5400°C (4 K/min)</li></ul>	v' = 12  ml/min
airflow	
1.2. Inertisation:	
N <sub>2</sub> flow	v' = 12  ml/min
Temperature	$T = 400^{\circ} \text{C}$
Duration	t = 3 h
1.3. Cooling to	$T = 180^{\circ}C$
N <sub>2</sub> flow	v' = 13  ml/min
(2) Feed	
Percentage volume of MBOH : hexane	95:5 vol%
Liquid feed flow through the capillary	$\nu' = 0.03 \text{ ml/}$ min
(3) Pressure of the gas supply (air and nitrogen)	
i.e., pressure over liquid feed	p = 2 bar
Pressure of the reactor system	p = 1.3  bar
(4) Temperature program for the gas	
chromatography	
Temperature start	50°C
Temperature rate $(dT/dt)$	10°C/min
Reached up to temperature	$T = 100^{\circ}C$
Holding time	$t = 12 \min$
(5) GC column	
Туре	Optima wax
Length	30 m
Film thickness	0.25 μm
Maximum temperature	$T_{\rm max} = 260^{\circ}{\rm C}$

TABLE 2: Conditions and parameters for characterization of different materials like natural zeolites by methyl butynol catalytic test reaction [95, 99].

incorporation of USY zeolites with platinum and palladium exhibited high catalytic activity [21]. Table 2 presents summary of conditions and parameters for the methyl butynol catalytic test reaction on natural materials [99, 102].

A good understanding of the operating parameters like reaction temperatures, reaction mechanisms, the conversion, selectivity, and the activation energy and more results about Thiele modulus are crucial factors in deciding on diffusion limitation and subsequently, will lead to a greater knowledge of zeolite coke formation during reaction [100, 101]. In addition, the implementation of the characterization method, the gas phase test reaction, methyl butynol (MBOH) as suggested in this article, will also lead to a better comprehension of the behaviour of active sites in their three existing forms: acidic, basic, and amphoteric reaction pathways. Gaining an in depth understanding of the acidic behaviour and catalytic activity of any solid material such as zeolite is important, and this includes features of kinetics reaction and reaction pathways together with the thermochemical structures of all zeolite types. Table 3 presents conditions and parameters for the temperature program desorption of ammonia [95].

In the long run, greater knowledge will inevitably result in the design of effective operational reaction conditions for local zeolite and in turn the optimum calibration of reaction temperatures and rate for coke formation. Correct theory using Saudi zeolite resource can lead to a better understanding

Conditions	Parameters
(1) Detector	
Thermal conductivity detector (TCD)	—
(2) Gas supplies	
Helium with a mixture of NH <sub>3</sub> in argon	5 vol.% NH <sub>3</sub> /Ar
(3) Sample amount	0.4 g
(4) Temperature program	
Temperature start	$T_{\text{Start}} = 25^{\circ}\text{C}$
Temperature rate (dT/dt)	20°C/min
Reached up to temperature	$T = 600^{\circ}\mathrm{C}$
Holding time	$t = 1 \min$
(5) Cooling temperature	$T_{\rm cooling} = 40^{\circ} \rm C$
(6) Sample saturations	7 vol.% NH <sub>3</sub> /Ar
Steam: helium with a mixture of NH <sub>3</sub> in argon temperature of sample saturation	$T_{\text{sample saturation}} = 40^{\circ} \text{C}$
Holding time	$t_{\rm holding} = 305  \rm min$
(7) Temperature increase	To 100°C
Temperature rate	20°C/min,
(8) Temperature desorbed $NH_3$ from the sample	T=100°C-400°C

of its behaviour when applied on industrial scales. This in turn will help to create the optimum operational conditions for the variety of industrial applications and greatly assist local product development in Saudi Arabia. The use of a combination of techniques for Saudi zeolite characterization and its coke formation during methanol conversion is recommended [103]. Methanol test reaction was employed to convert hydrocarbons, either gasoline range (MTG) or light olefins (MTO) on zeolite type ZSM-5. In addition to methanol gas phase test reaction, other techniques were also used to attest to the successful synthesis of zeolite, like neutron spectroscopy, nitrogen adsorption-desorption, and nuclear magnetic resonance spectroscopy [103].

The benefit of utilizing local Saudi zeolite has a number of advantages. Firstly, it will likely reduce industrial operational production costs and secondly such use will add greater value and benefit local enterprise and the economy. In terms of production costs, Saudi zeolite is of course cheaper to source locally, and huge savings can be made on transportation and on the cost of importing zeolite from overseas. Additionally, using local zeolite in production will encourage greater interest in its research in academic institutions in Saudi Arabia together with the collaborative projects, which may potentially be established with institutes worldwide. Such future research should lead to the discovery of novel, beneficial methodologies and procedures for zeolite modification such as those suggested in this article [38, 100, 101, 103]. The end goal is to gain a more detailed understanding and information about the structure, active sites, and chemical properties of local modified zeolites. Understanding how local zeolite can be modified for better economic return will also indirectly benefit other areas such as energy production, water quality, manufacture of polymers/plastics, and the environment. This article will further discuss and furnish some insight into zeolite polymer research. A recent study [104] reported how the zeolite type, clinoptilolite, had been modified and further illustrated its role in the adsorption energy, heat adsorption, and activation energy.

Another pioneering work [98] demonstrated the use of modified zeolite for water desalination and treatment. Zeolite was shown to have been successfully modified with the addition of the surfactant N,N dimethyl dehydroabietyl-amine oxide (DAAO) in the presence of calcium cations and magnesium ( $Mg^{2+}$ ) on the zeolite framework structure [105]. From this investigation, the desired application was directed to remove humic acid (HA) for potable water. Since HA can adversely react during the chlorination and in the process, produce unwanted by-products, its removal indirectly maintains the quality of drinking water. The study findings [105] are supported by thermodynamic and kinetics interpretations and attest to the reaction rate conditions [105].

The local Saudi natural zeolite exhibits low surface area and their modification to nanosize increases its surface properties [74, 75], and further investigation into the thermodynamic and kinetics properties of the material for its potential use in industrial applications is clearly warranted together with a comparison with previous thermodynamic studies on similar zeolite resources [106].

Notably, zeolite was employed on membrane applications for the purpose of water desalination and another newer study directed a modified zeolite for carbon capture [21]. Research and investigations with the aim of discovering the optimum zeolite material for seawater desalination is ongoing. A modified form of zeolite was synthesized through the polymerization of the anilinium cation in a zeolite structure [107]. In such a way, anilinium cation was inserted synthetically into zeolite for the purpose of chromium (VI) adsorption from an aqueous solution. A variety of instrumentation techniques were employed for the structure characterization of the fabricated sample and with the aim of verifying its successful adsorption to chromium (VI) [107]. They are Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (H-NMR) spectroscopy, X-ray powder diffraction (XRD), thermal gravimetric analysis (TGA), and scanning electron microscope (SEM) [107, 108]. Nanocomposite polymer-zeolite material was also synthesized for water fabrication [109].

In recent years, researchers [110] have shown that polymer-zeolite is a suitable material for manufacturing applications of plastic products [110]. The characteristic channel structure inherent in the dimensional framework structure of silica-alumina facilitates a smooth synthetic insertion of cations of metal thereby resulting in an enhanced zeolite modification [111]. The goal of synthetically combining zeolite and polyethylene glycol [111] is to reduce the volume of plastic and to replace the glycol with an alternative material such as zeolite.

Currently, the potential use of polymer-zeolite composite in the manufacture of plastics is realistically viable since recycling plastics is problematic and costly. In this way, its use would likely lead to a further reduction in the volume of waste plastic worldwide together with a positive impact on the environment. In order to become effective, comprehensive

methods for combining zeolite with plastics in the promotion of efforts in recycling plastics need to be established. Recent investigation [111] is addressing the issue, and attempts to find combinations of zeolite and polyethylene glycol in the manufacture of environmentally friendly plastic packaging products is currently underway. Similar research and testing for the modification of local zeolite is required in Saudi Arabia in a period when the petrochemicals industry sector is developing continuously and where greater economic diversification has been prescribed [111]. It is predicted that the correct exploitation of local zeolite resource will inevitably lead to the successful production of eco-friendly plastic packaging products in the Saudi Arabian context [74]. Also, note that petrochemical based plastic is a commercially attractive industry due to the low cost of the variety of manufacturing processes [35, 110]. More recently, a polymerzeolite (MFI) mixed matrix membrane was developed [112] in relation to a membrane model. This newly fabricated composite polymer-zeolite showed great potential together with an effective capacity for the adsorption of gases like methane and carbon dioxide [112]. The fabrication of zeolites can be achieved by direct synthesis [113], sol gel method [114], or by a nonhydrothermal process [115, 116].

Heterogeneously catalyzed dehydration reactions have long been investigated. However, the mechanism of these reactions is not fully understood. Pines and Pillai [62] suggested that with regard to zeolites, both acidic and basic centers are required for the dehydration of alcohols on an H-ZSM-5 and have been studied in particular [70–72]. On the other hand, the preparation of dienes starting from diols on a heterogeneous basis represents a less well-developed topic. Especially in the liquid-phase dehydration of HG with the aim of forming the 1,3-diene, the homogeneous catalyst is mainly used. In the heterogeneously catalyzed condensation reaction between glycerol and acetone, the literature mainly mentions ion exchange resins [54, 57].

Overall, studies conducted on the properties of natural Saudi zeolites have shown huge potential for its use in industrial applications in energy production as a catalyst due to its excellent absorbency. The potential broad application of Saudi zeolite will prove to be of great value in a variety of local industrial settings for example in the production of photocatalyst pollutants degradation and environmental ecofriendly polymer applications. Therefore, based upon the wider literature review [102, 106, 117–119], this article also recommends the utilization of a greater variety of characterization techniques on the local materials in Saudi Arabia such as pyrrole adsorption [120], temperature-programmed desorption of ammonia and temperature-programmed desorption of carbon dioxide [102], and isopropanol methyl butynol test reactions [102, 118, 121]. By employing these additional methods, the details and descriptions of catalytic activity together with the clear demonstration of their acidic or basic properties may be better understood [89, 91]. As a result, more efficient methods can be provided in the modification of local Saudi zeolite materials for use in a greater range of industrial production applications such as the coke formation. Studies were performed to understand challenges of the coke formation on other type of zeolite like H-ZSM-5 zeolite [87] during the conversion of dimethyl ether to Olefins. The problems of coke formation on H-ZSM-5 zeolite [87] during conversion of dimeththyl ether to olefins have been researched with particular attention to process variables in the coking and rejuvenation of the zeolite catalyst in the fixed bed reactor [122]. They include mesopores matrix material, temperature, space time, catalyst acidity, and steam [87, 122]. Catalysts samples were characterized in two ways: N2 adsorption-desorption and temperature-programmed oxidation. Coke fractions (3 types) were shown to be deposited in microspores, on the surface of zeolite and in the matrix mesopores. In the zeolite microspores, coke formation is reduced and in the main is due to a combination of low Si/ AL ratios [122], a 350°C temperature together with cofeeding water with DME. In this way, the stability of the catalyst is maintained. When the heating ramps up to 550°C, the catalysts recover the activity entirely through combustion. This is confirmed by reaction and regeneration cycle [122]. Obviously, understanding the catalytic activity and behaviour of active sites before and after regeneration for the local samples has not yet been studied. Hence, performing more investigations in this direction to explore the knowledge also contributes in developing better routes for the stability of local zeolite samples during the reactions, and the coke formation reduction especially that the coke formation phenomena continues to be a worldwide challenge for many petrochemical industries.

The effects of the treatment of MFI (H-ZSM-5) with acid (H<sub>3</sub>PO<sub>4</sub>) or basic (KOH) was examined, and the catalytic performance was compared with the structural and catalytic aspects of the zeolite after treatment with the help of cracking of 1-butene under steam for a period of five hours [123]. The results reveal a decrease in the 1-butene conversion with an increase in propylene selectivity. The sample was treated with the acid (H<sub>3</sub>PO<sub>4</sub>) [124]. However, an additional type of modification was also revealed with basic KOH in that it showed an increasingly higher level of the selectivity of propylene for samples with zeolite that contains a greater ratio of silica to alumina and high K. Treatment with acid (H<sub>3</sub>PO<sub>4</sub>) and basic KOH resulted in the formation of mesopores in the silicalite-1 [124]. For the treated sample, the diffusion length was decreased with the KOH. As a result, desilication occurred. This caused a reduction in the length of coke precursors and led ultimately to a lessening of the diffusion of these species [119]. Furthermore, methanol-toolefins (MTO) reaction has also received attention from other scientists to test the catalytic performance of both H-ZSM-5 and a modified form of zeolite H-ZSM-5 with magnesium. It has resulted in a higher selectivity of olefin and increased longevity due to a decrease in the formation of active sites [119].

Moreover, Konno et al. [125] showed a more effective procedure on ZSM-5 catalyst for producing better yield of light olefins. Konno et al. [125] investigated the model of naphtha compounds: cyclohexane, methylcyclohexane, and n-heptane over ZSM-5 in the kinetics of catalytic cracking. It was established that this catalytic cracking followed firstorder kinetics [125]. Alkane concentrations and activation energies were found to be 119, 116, and 126 kJ mol,

respectively, for cyclohexane, methylcyclohexane, and n-hexane cracking over nano-ZSM-5 (crystal size = 100 nm), much higher than those known for conventional catalyst (macro-ZSM-5; crystal size = 2 mm). The Thiele modulus and the effectiveness factor were established in the rate limiting step [126] in the cracking process. First, cracking using nano-ZSM-5 was conducted under reaction-limiting conditions. Secondly, however, reaction using macro-ZSM-5 at 923 K was carried out under transition conditions between reaction and diffusion limiting steps. Additionally, the catalytic cracking of a model naphtha feed was executed by applying Nano-ZSM-5 on macro-ZSM-5 [126]. In addition, fluid catalytic cracking process (FCC) process requires braking C-C bonds to more important chemical fractions, and it requires materials like Y zeolite with a strong Brønsted acidity property [127]. On other hand, a future prospective and policy for utilizing local zeolite resources can be achieved by a good combination between Si/Al of the various forms of local zeolites to produce 2D and to minimize the

In the literature [129, 130], two examples of zeolite modification were found using two types of zeolite: delaminated and pillared. This investigation [129, 130] demonstrated a proportional correlation between acid sites and catalytic activity. The results show that the entire surface of the first delaminated type is catalytically active, whereas the active sites on the second pillared type dilute and remain inactive. The functionalization of inorganic pillars is limited though organic ones provide good acidic or basic sites with or without functionalities [131].

formation of coke [128].

An ion exchange method was proposed to modify local Saudi samples [75]. An additional article suggests further development of local zeolite resources to synthesize frameworks of zeolite (2D/3D) by approaching standard solvothermal methods [132] through connecting zeolite monolayers with various surfactant-templated nanosheets [133, 134] considering also the demand that commercial applications will serve.

On other hand, in the literature [74, 75], the modification of natural Saudi natural clinoptilolite zeolite samples using the various processes of nanoformation was proposed for energy application. In contrast, researchers from outside Saudi Arabia [135] investigated the removal of heavy metal ions from wastewater by a synthetic natural clinoptilolite [135]. The synthetic clinoptilolite was then modified through a pretreatment with solutions of 1.0 mol/L NaOH, KCl, HCl, NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> [25]. Results showed that a significant adsorption of heavy metal ions from wastewater like Zn<sup>2+,</sup> Pb<sup>2+,</sup> Cd<sup>2+,</sup>, and Cu<sup>2+</sup> was achieved on the NaClmodified clinoptilolite sample [135]. In addition, the Langmuir model has been found to be as a more efficient model for describing the adsorption behaviour of the NaClmodified clinoptilolite [135]. Other studies [136-139] showed a synthesis of natural clinoptilolite under diffident reaction temperatures that ranged between 120°C and 200°C [136-139]. In the example, synthesis of Na-clinoptilolite occurred at temperature ranges 100°C to 140°C. Synthesis of K-clinoptilolite was achieved at higher reaction temperature about 195°C [137].

Moreover, further study and exploration is proposed for our proper understanding of new forms such as 2D/3D zeolites [140] and the mechanochemical effects on the zeolite structure. Moreover, zeolite structure can be further examined by using techniques like nuclear magnetic resonance (NMR) [140]. To the best of knowledge, no studies for the crystallographic structure entirely performed on developed forms of the local samples have been reported using NMR. Dawson et al. [141] and their coworkers developed a more accurate way for abstracting accurate information about crystallographic structure of Silica zeolites using the NMR technique. Correlation between calculation of the density functional theory (DFT) for Si(OSi(OH)<sub>3</sub>)<sub>4</sub> clusters and zeolitic SiO<sub>2</sub> frameworks was successfully achieved [141]. The advantage of employing the proposed method is that results show more accurate structure integrations. A similar approach to the local Saudi zeolites can be also implemented on local samples' elucidations, nucleations, crystals formation, pore size, and rearrangements [141].

Local zeolite that has been modified has more uses in commercial applications over and above those already proposed in the literature energy [75]. Metal-organic framework zeolites (MOF) of two or three dimensions (2D/3D) offer greater advantage and are more effective compared to natural zeolite. This is due to improvement in the surface area of the 2D/3D types. Subsequently, a better approachability to 2D and 3D active sites minimizes the blockage of pore sizes during catalytic reactions and also leads to a decrease in the formation of coke. An example of the commercial use of metal-organic framework zeolites (MOF) with two/three dimensions is shown in the following polymeric membranes' application [127, 142]. Here, high quality membranes are effective in the separation of mixtures of xylene isomer [143]. Also, a number of silicate-1 membranes present activation with temperature for the presence of single H<sub>2</sub> [127]. An eco-friendly alternative to the cryogenic process including the adsorptive and adsorptive reaction processes is to use gas separation with membranes. It also has the advantage of saving energy, and it is relatively straightforward to integrate membrane units into other types of separation and reaction processes [144].

Today, a number of polymeric applications have commercial viability and have produced good results. The advantage is that such applications are based on polymeric membranes. The examples are producing nitrogen from air, recovering H<sub>2</sub> from ammonia purge gas, removing carbon dioxide from natural gas, and separating hydrocarbons in the process of enhanced oil recovery (EOR) [144]. In addition, the Ca<sup>2+</sup> clinoptilolite exhibits the best ability for  $CO_2/CH_4$  separations because of its higher selectivity [145].

The limitation of using conventional polymeric membranes is to compromise productivity with efficiency and vice versa in that solution-diffusion mechanism results in concessions to either permeability (limiting productivity) or selectivity (affecting selectivity) [146]. This is Robeson's upper bound [147]. In order to overcome such drawback, the employment of membranes based on a selection of pore sizes is required since membranes have the capacity to separate molecules according to their size and shape [147, 148].

# 4. Proposed Future Plans for Local Natural Clinoptilolite

- (i) Development of the local zeolite to a higher surface area, for removing carbon dioxide from natural gas and separating hydrocarbons in the process of enhanced oil recovery (EOR) [144, 149].
  Figure 6, presents protocol for modification, treatment, and characterization of natural Saudi clinoptilolite zeolite for environmental application.
- (ii) Treatment of local zeolite with acid ( $H_3PO_4$ ) or basic (KOH) is one option for the future examination of local zeolite. After that, it will be fruitful to study the effect of treatment on their catalytic performance and products selectivity using MBOH test reaction [150]. Indonesian natural zeolites were treated with HCl and  $H_2SO_4$  [151]. The treatment led to an enhancement in the natural zeolites' adsorption capacity and stability and generated suitable adsorbent for gas or liquid separation [151].
- (iii) Comparison of the results of investigations with other findings is necessary, as proposed in Figure 6. In addition, the identification of the active acidic centers by temperature-programmed desorption of ammonia is required.
- (iv) Based on previous studies [87, 100, 101, 103, 122, 128], local investigation of natural clinoptilolite by acid or base treatment is required in order to gain a complete understanding of its properties and in discovering ways to exploit them and use the local zeolite in a variety of industrial applications such as in coke reduction. Performance of kinetics and thermodynamics investigations will be necessary to examine the diffusion limitation for the new formed nano local zeolite.
- (v) Conversion of MBOH with water on an acidic catalyst could be established at a lower temperature. The conversion of MBOH with water [106] on the local zeolite at reaction temperature like 120°C might also be of interest for investigation for retarding the coke formation on the local zeolites [122].
- (vi) Moreover, it is believed that metal oxide zeolites composites [152] can be altered to become potential materials for SO<sub>2</sub> removal from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel, and fuel oils. For this future objective, it is necessary to target the ability of the local nano modified local zeolite towards the SO<sub>2</sub> adsorption from crude oil. First, adsorption of the process for traces followed by regeneration of modified zeolites in hydrogen (steam process) has the advantage that the hydrogenation of sulfur containing heterocompounds takes place in the absence of the oil fraction so other aromatic compounds are not hydrogenated.



FIGURE 6: Proposed test protocol for modification, treatment, and characterization of natural Saudi clinoptilolite zeolite for environmental application.

### 5. Summary

In sum, results of this review shows that kinetics modeling for the clinoptilolite zeolite is needed in order to establish the objective for minimizing coke formation during steam reactions. The chemical weight percentage compositions of natural local Saudi zeolite compared with natural clinoptilolite sourced worldwide have also been reviewed. It was found that the percentage weight chemical compositions of the clinoptilolite zeolite are close to that of other international sources. There is a good correlation of silica to alumina ratio. However, the Japan sample of natural clinoptilolite zeolite is the highest and contains additional elements namely P2O5, S, CO2, and H2O. Moreover, various modification methods of zeolites were presented in the literature [105] by a variety of means: physical, chemical, and composite modification. They constitute the knowledge foundation or guidelines for academics and researchers in Saudi Arabia upon which the most viable modification

methods can be devised in relation to its own local zeolite resources and to the efficiency of the nation's future industrial applications such as the environmental sector. More specifically, this current article concludes that in order to fully explore and understand the catalytic behaviour of active sites specially the acidic centers (during and after reaction) and the coke formation and its deactivation, a greater variety of characterization techniques need to be employed.

### Abbreviations

FCC:	Catalytic cracking
MTG:	Methanol-to-gasoline
EDTA:	Ethylenediaminetetraacetic acid
HG:	Hexylene glycol
UV-Vis spectroscopy:	Ultraviolet-visible spectroscopy
XRF:	X-ray fluorescence
MBOH:	Methyl butynol

TCD:	Thermal conductivity detector
DTA:	Differential thermal analysis
TGA:	Thermal gravimetric analysis
SEM:	Scanning electron microscopy
XRF:	X-ray diffraction
TPD of pyrrole:	Temperature-programmed
	desorption of pyrrole
EDX:	Energy dispersive X-ray
	spectroscopy.

## **Conflicts of Interest**

The author declares no conflicts of interest.

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