

Composite Zeolitic Material Synthesis And Its Functionality Synergism: A Review

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Abstract—The discovery of a novel family of molecular sieves which is obtained by impregnation and/or incorporation of different porous materials together, has aroused interest in the field of porous materials. Composite zeolites is a material which are sometime a hierarchical structured materials such as micro/mesoporous composites or non-heterogeneous composites such as meso/mesoporous or micro/microporous structure, which is either having two different Zeolites phase or a zeolite and a non-zeolite phase. The composite zeolitic based materials find applications in adsorption, host-guest encapsulation, and many different petroleum derived chemical processes such as catalytic cracking, gas conversion process, hydro-cracking, isomerism, aromatic alkylation among others. This report is intended to review and briefly summarise the current achievements and outline the recent work in the field of composite zeolites

Keywords—Composite, Zeolites, Microporous, Mesoporous, Porosity, Hierarchy, non-zeolite phase, catalysis.

INTRODUCTION

Zeolites are a family of microporous aluminosilicate material linked with oxygen atom and possess open frame work structure with three dimensional tetrahedral units creating a network of uniform pores and cavities having microporous regular structure and molecular dimensions[1].

Zeolite are known to have various uses and functions in industrial application such as adsorption, chemical synthesis, catalysis, product separation and in petrochemical processes due to their unique properties. These properties include pore structure, adsorption capacity, acidity, high thermal stability, separation properties, shape selectivity and polarity[2]. Zeolite is widely used as heterogeneous catalyst in different petroleum derived chemical procedures (e.g. catalytic cracking, gas conversion process, hydrocracking, isomerization, aromatics alkylation, methane to gasoline De-waxing, adsorption refrigeration application, cracking, fischer-Tropsch process, waxes to clean biofuels, removal of dye from aqueous solution. This functionalities can be further improved by manipulating the ratio of different phase

zeolites alongside changing their synthesis conditions [3].

It has been recognized that the size of zeolite particle has extensive effect on its catalytic performance, especially in reactions dealing with external surface and inhibited by a diffusion process [1], however with the introduction of hierarchical pore systems, the diffusion related problems in a zeolite composite synthesized has been greatly tackled.

Great emphasis has been directed towards the production of different variety of composite zeolite, the main purpose is to obtain an heterogeneous catalysts with improved performance. Composite zeolite can either be hierarchical pore structured such as micro/mesoporous composite or non-heterogeneous as micro/microporous [4]. Composite zeolite are important because the lapses of one zeolite type is compensated by the other, for example the acidity of β -zeolite is not strong enough while ZSM-5 lacks good performance in the transfer of aromatic due to its small pore size causing low rate of molecule transfer into the pore of the zeolite catalyst [5], therefore to improve the performance of zeolite catalytic material to meet the requirement needed for industrial application, effort has been directed on the synthesis of multi-structured complex catalytic material hence the need for this review.

Non-Zeolite/Zeolite Composite

Different work has been carried out on the synthesis of non-zeolite/zeolite composite. It is a composite that composes of zeolite and another element most often metals, transition metals and aluminum giving it distinct catalytic properties when incorporated into zeolite frame work. It is advantageous to insert this transition metal/other related metals by direct synthesis because it leads to high dispersion of the metal in the zeolite structure, however this process is complicated and will depend on the synthesis conditions such as presence of cations, pH and source of metal used.

Traditionally, cationic metal can be incorporated in the large or extra-large pore zeolite by cationic exchange [6], impregnation [7] or chemical vapor deposition [8], of the metal precursors after zeolite crystallization. These post-synthesis processes needs a lot of steps to obtain the expected metal containing zeolite, it is also characterized by the non-uniform distribution of the

metal in the cavities and channels of the zeolite. There are also limitations to the effective diffusion of the metal into the small zeolite depending on its ionic radius, all these drawback make direct synthesis of metal containing zeolite in extra frame unique and it provide a better substitute since it eliminates the multi-step methodology making the process more economical, and attractive to industry. These direct method also has its limitations since it is highly dependent on the zeolites synthesis conditions, the metal precursor, and the metal stability under these condition

An example non zeolite composite is the synthesis carried out by Zendehele *et al* 2014 [9] which indicates that TiO_2 is capable of oxidizing a range of organic compounds into harmless compounds such as CO_2 and H_2O . nano particles of TiO_2 exhibit distinctive properties different from bulk TiO_2 particles but are instable and have the likelihood of the primary nanoparticle undergoing aggregation at neutral pH into grains of much larger size with inconsistent distribution and age changing it property over time. This is remedied by encapsulating nanoparticles of TiO_2 inside the internal void of zeolite that are nanometer scale. The incorporation of TiO_2 cluster into zeolite allows one to prepare photocatalyst with a range of distinctive activities. TiO_2/NaY zeolite was synthesise using the following materials; Aluminum hydroxide, silica gel, sodium hydroxide, calcium chloride ($\text{Ti}=\text{O}$) $\text{K}_2(\text{C}_2\text{O}_4)^{2-} \cdot 2\text{H}_2\text{O}$ and methylene blue (MB) dye, NaY zeolite having a molar ratio of $16\text{NaOH} : 1\text{Al}(\text{OH})_2 : 1.15\text{SiO}_2 : 3.20\text{H}_2\text{O}$ was synthesized [10] and characterized with X-ray diffraction. TiO_2 was then incorporated into NaY zeolite by stirring NaY zeolite (10g) at ambient temperature with a solution of $\text{K}_2(\text{C}_2\text{O}_4)^{2-} \cdot 2\text{H}_2\text{O}$ or $(\text{NH}_4)_2(\text{Ti}=\text{O})(\text{C}_2\text{O}_4)^{2-} \cdot 2\text{H}_2\text{O}$ at required concentration (0.05, 0.4 and 0.8) for 4h, the solid was then filtered and washed using a freshly prepared 0.5M aqueous solution of CaCl_2 and dried in an oven at 150°C for 5h. The composite was characterized using X-ray diffractometer alongside X-ray spectroscopy, the result showed that the TiO_2 was incorporated onto NaY without any change in the crystalline structure of the host NaY zeolite. These composites have many advantages such as high stability and high porosity. The photocatalytic degradation behavior of methylene blue was investigated for TiO_2/NaY zeolite. The effect of time, initial concentration, temperature and pH of methylene blue (MB) on its degradation was studied using UV-spectroscopy, the optimum conditions were 8h time, high initial concentrations of methylene blue and photocatalyst, and basic pH. Pure zeolite material may not be effective as a photocatalyst but composite zeolite as TiO_2/NaY zeolite can be effectively used because it combines the photo generative role of TiO_2 which are highly oxidizing and the catalytic, absorption property of zeolite which makes it a suitable photocatalyst for the removal of methylene blue. However direct synthesis method would have been a better option than the substantial ion-exchange and decomposition used.

Also the work of Yuni K *et al* [11] focuses on the synthesis and characterization of meso type ZSM-5 aggregates impregnated with metallic cobalt, these served as an active catalyst for the oxidation of the methane to the methanol and formaldehyde. Higher external surface area of mesoporous ZSM-5 zeolite accommodated a higher number of CO_3O_4 and CoO species, which resulted in a higher overall selectivity to methanol. The amount of methanol increased linearly with increasing external surface area of the zeolite. The material used for the synthesis were tetrabutylammonium hydroxide, TPAOH (Sigma-Aldrich), tetraethyl orthosilicate, TEOS 99% (Shintetsu), NaOH (Merek), acetic acid, poly (diallyldimethylammoniumchloride), PDDA 35% wt (Aldrich), aquademin. Mesoporous ZSM-5 was synthesized using the procedure reported by Wang *et al* (2010) with some little adjustments. Using a molar composition of $7.84(\text{TPA})_2\text{O} : 1\text{Al}_2\text{O}_3 : 50\text{SiO}_2 : 2301.74\text{H}_2\text{O}$ gel of ZSM-5 was prepared. This was stirred and aged for 3 h at 100°C , 1 g PDDA, (35% wt.) was added to the reaction mixture. After 15 h stirring at room temperature, the mixture was put in an autoclave where crystallization took place at 150°C for 144 h. The product was washed, filtered, dried at room temperature, and calcined for 5 h at 550°C to eliminate organic template. An amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with initial wetness was added to 1 g of as-synthesized Na-ZSM-5 to attain 2.5% wt $\text{Co}/\text{ZSM-5}$ mdt. For 24 h the mixture was then mixed thoroughly. The impregnated sample was dried overnight in air at 100°C . The XRD pattern and SEM images showed of zeolite was successful to form ZSM-5 structure and ESD measurement confirmed that the template was completely removed after the zeolite was calcined at 550°C leaving a structure of both mesoporous and microporous channel. The catalytic test revealed that the catalyst is considerably reactive in converting methane to methanol due to the presence of cobalt oxide species in the meso-channel of the structure, It has also been revealed that Socony-Mobil Company. used additions of chrome oxide for activating coke burning, a process used on large scale for the activation of zeolitic catalysts.

The preparation of mesoporous zeolite is essential as seen in the above synthesis owing to the fact that the microporous zeolite exhibit restricted pore size (1nm) which induce some diffusion problem when bulky reactant or product are used in specific catalytic application, especially those related to oil upgrade and synthesis of fine chemicals. The application of mesoporous materials, which show pore openings higher than 2nm has been successful owing to their low hydrothermal stability, therefore to improve the pore accessibility of zeolite creating secondary mesoporous system within the microporous zeolite matrix is necessary, in the preparation of hierarchical material containing micro and mesoporosity [12]. Different approaches can be followed to create mesoporosity in zeolite. The most common method used is based on synthesis modification called destructive strategy where the mesopores are created

by selective extraction of atoms, mostly Si or Al from the zeolite frame work, these desilication or dealumination involve post synthesis procedure such as calcination, steaming, acid leaching or chemical treatment as used in the Co/ZSM-5 zeolite case above, nevertheless very important advancement has been made in this field and direct or "one-pot" synthesis of hierarchical structures have proved more suitable since it involves a reduced number of step therefore attractive to industrial application if the mesoporous template were inexpensive or could be recycled. Shortening the diffusion distance in the zeolite crystal is the best solution to utilize the intrinsic properties of the zeolite to the fullest, and many synthetic and post treatment approaches are being explored to realize this. The incorporation of the nanosized zeolite structures in meso- and macroscopic bodies may alleviate the diffusional resistance in the zeolite, but those in the catalyst particle may remain, for which diffusion measurements remain essential.

A work by Taher et al [13] presents the loading of zeolite with nano iron oxide prepared using a simple chemical route. Zeolite with its well defined structure and microporous cavities work as a good candidate for nanoparticles support and hosting. The interaction of nanoparticles in both form of metal and metal oxide with zeolite has opened a new window of applications such as sensors, electronics and magnetic applications. It was reported that zeolite exhibit magnetic property by its loading with CO. The zeolite composite was prepared as follows, an exact amount of NaOH solution was added to Pyramid sodium silicate under stirring at room temperature, a mixture of NaAlO₂ and TPAOH solutions were added sequentially with continuous stirring. The reaction was stirred for at least 2 hours and transferred to a 250 ml Teflon-lined steel autoclave. Then reaction was left at 170 °C under pressure for 24 h. The product obtained was filtered, washed using deionized water, dried, and calcined for 8 hours at 540 °C to remove the template, a certain amount of Iron chloride equal to obtain final loading of 1% and 2 % Fe₃O₄ was added to distilled water, and stirred for 30 min, 2 g of calcined zeolite was added to the solution above after heat treatment at 150 °C under vacuum throughout the night. The mixture was kept at 80 °C under continuous stirring for a period of 6 hours with reflux. The mixture obtained was then transferred to a rotary evaporator and water was evaporated completely. The obtained composite was dried in air for 8 hours at 70 °C. The prepared nanomagnetite has a uniform particle size of 4- 6 nm, the X-ray diffractometer proved that the formed magnetite is a cubic Fe₃O₄. It showed also the possible incorporation of formed magnetite within the frame work of zeolite, VSM study showed a sharp decrease in magnetic power that has been observed upon the loading of magnetic nanoparticles on zeolite. Zeolite acquire magnetic properties after doping with Nano iron oxide.

In another work on zeolite modification with non zeolite, zeolite was modified by polyaniline through

the process of polymerization of anilinium cation in the outside of the zeolite channels in the work by Abdulsalam et al [14].

Nanocomposite of polyaniline/zeolite (PANI/Zeolite) was attained by oxidation polymerization of anilinium cation with the zeolite structure. The synthesis process of PANI/Zeolite nanocomposite was done via in-situ oxidation polymerization in which natural zeolite was grounded and sieved with 100 µm of sieve, then 15g of zeolite was vigorously stirred in 200ml of 1M HCl for 24h, 10 g (107mmol) of aniline was dispersed in mature of HCl and zeolite with continuous stirring for 24h, ammonium persulphate (67mmol) was dissolved in 1M HCl (200ml) and dropped into the beaker, the mixture was kept at constant stirring and the solution is placed inside an ice bath maintaining stirring for another 24h, when the reaction was completed the dark green precipitate resulting from the polymerization reaction was filtered and washed with distilled water, acetone and methanol sequentially in order to remove the excess of initiator monomer, and oligomer. The precipitate was then dried overnight in vacuum oven at 60°C, the prepared PANI/Zeolite was characterized by FTIR and XRD and confirmed the incorporation of polyaniline in the zeolite channel, SEM image confirm the nanometer size range of polyaniline chain in zeolite channels. The adsorption performance of PANI/Zeolite nanocomposite was studied for the removal of hexavalent chromium, and the result showed the adsorption percentage of Cr (vi) increases rapidly with increasing adsorbent concentration offering greater surface area also the adsorption capacity was found to be increasing with increase in the concentration of Cr (vi), the maximum adsorption of Cr (vi) occurred at pH 2.6 and decreases at high pH value.

Generally, the synthesis of the non-zeolite/zeolite composite, introduces a wide range of application which includes its use as a photocatalyst, and as an adsorbent and also gains magnetic attribute respectively, revealing that zeolites could be incorporated with suitable element due to its porous nature in order to serve specific purposes. It is also observed that nano and mesoporous zeolite are preferred to microporous zeolite, the former presents large surface area with reduced molecular radius (reducing the travel time of molecules into the zeolite pore) and the latter offers large surface area with pores large enough to be accessed by bulk molecules, compared to the microporous zeolite with large surface and small pore size limiting the easy access of bulk molecule. [11]. Mesoporous zeolite also enhance the incorporation of large molecule size metal into the zeolite frame work but mesoporous zeolite are unstable therefore the concept of hierarchical zeolite become handy and pore size and shape is selective over wide range of sizes.

Zeolite/Zeolite Composite Catalyst

Composite zeolites with binary structure not only combine the advantages of the two distinct kinds of

molecular sieve, but also induce the formation of special properties which can improve its catalytic performance. Thus exploration of new composite zeolite systems attracts more and more interest in scientific and industrial field [15]. This review focuses on a few of these composite zeolite which includes; MCM-49/ZSM-35, ZSM-5/Rectorite, ZSM-5/ β co-crystalline, ZSM-5/hollow β , ZSM-5/MCM-41, MAZ/ZSM-5, Pd/ZSM-5/MCM-48, ZSM-5/SAPO-34 composite zeolites.

Sujuan Xie *et al* [4] showed the effect of structure directing agent, influence of $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio and the effect of crystallization time on the synthesis of MCM-49/ZSM-35 composites, where the molar ratio of the two structure directing agent used (CHA and HMI) determine which zeolite is synthesized. Pure MCM-49 zeolite was synthesized with mole ratio of CHA/HMI equal to 1.0, an increase in the content of CHA leads to the appearance of ZSM-35 phase, while a molar ratio of CHA/HMI reaching 4.0 gives pure ZSM-35 zeolite, changing the molar ratio from 2.3 to 3.0 provides a new route for the synthesis of MCM-49/ZSM-35 composite zeolites. Further adjusting the molar ratio of $\text{Na}_2\text{O}/\text{SiO}_2$ may provide another way to produce MCM-49/ZSM-35 composite zeolites with different compositions.

The synthesis and characterization was done as follows; commercial chemicals used for the synthesis process include silicasol (25.59 wt.% SiO_2 , 0.31 wt.% Na_2O , 74.1 wt.% H_2O , sodium aluminate solution (16.9 wt. Al_2O_3 , 24.2 wt.% Na_2O , homemade), sodium hydroxide (96 wt.% NaOH), hexamethyleneimine (HMI) (98 wt.%), cyclohexamine (CHA) (99.5 wt.%) and deionized water. Initial gel with molar composition $3.0 \text{ Na}_2\text{O}:1.0 \text{ Al}_2\text{O}_3:30 \text{ SiO}_2:10 (\text{HMI} + \text{CHA}):900 \text{ H}_2\text{O}$ was aged at 80°C for 4 h and then increased to 166°C for crystallization. With time, solid products were gotten by centrifugal separation and washed with deionized water until pH 8–9. The samples gotten were dried at 120°C to obtain as-synthesized zeolites, and calcined at 538°C in air to form calcined zeolites free templates. To obtain fully exchanged H-type zeolite the samples undergo ion exchange with a 0.8 M aqueous solution of ammonium nitrate at 80°C for three times, then dried at 120°C and calcination at 520°C . The structure characterization, acid distribution and morphology of the as-synthesized MCM-49/ZSM-35 composite zeolites were characterized by X-ray diffraction, N_2 adsorption isotherms, NH_3 -TPD, scanning electron microscopy (SEM) as well as HP-129Xe NMR technology. These characterizations give obvious different pore structure of the MCM-49/ZSM-35 composite zeolites from the mechanical mixing counterpart.

Tianbo Zhao *et al* [5] in their work pointed out that there is a significant difference in the co-synthesis of two zeolite phase from their homogenous physical mixture when using chemically pure Sodium aluminate (NaAlO_2), ammonia water, sulfuric acid, commercial grade Silica sol and TEAOH, the synthesis was carried out by taking certain amount of ZSM-5 crystal seeds and mixed homogeneously with

0.6g sodium fluoride, 29.5 g 15% TEAOH, 2.2 g 20% sulphuric acid solution and 13.5 ml deionized water, 0.5 g NaAlO_2 was then added and stirred till it was homogeneous, 19.7 g silica sol was also added and stirred physically until it was homogeneous. The sample was put in an autoclave and left to crystallize at 140°C for 6 days. After crystallization the mixture was rapidly refrigerated, filtered, washed, then calcined at a temperature of $100\text{--}110^\circ\text{C}$ for 3–4 h to obtain ZSM-5/ β zeolite co-crystalline base powder.

The XRD characterization indicated that ZSM-5/ β co-crystalline zeolites could be synthesized, scanning electron morphology (SEM) also showed that the morphology of ZSM-5/ β co-crystalline zeolite are irregular spherical shaped similar to β zeolite, unlike their physical mixture they didn't grow together disorderly, proving that ZSM-5/ β co-crystalline zeolites was not just a homogeneous mixture of ZSM-5 and β zeolite. NH_2 -TPD characterization pointed out that ZSM-5/ β co-crystalline zeolite had strong acid amount which was 3% more than that of their physical mixture. N_2 adsorption characterization indicated that both ZSM-5/ β co-crystalline zeolite and their physical mixture had little deviation in their pore structure. Comparing the catalytic activity of ZSM-5/ β co-crystalline zeolite to that of their physical mixture in toluene alkylation to give xylene. ZSM-5/ β co-crystalline zeolite gave high xylene content which was 10.5% than that produced by their physical mixture and this justify that ZSM-5/ β co-crystalline zeolite has better selectivity for toluene alkylation.

A similar work was done by Qing Hu Zeng *et al* [15] on the Growth of ZSM-5 crystals within hollow β -zeolite but in this case the synthesis procedure was different, it took advantage of the aluminum-poor interior and aluminum-rich outer rim of β -zeolite crystals, the extraction of silicon will be favorably in the aluminum-poor bulk rather than the aluminum-rich external surface because a high framework Al concentration will hinder Si extraction, while a low Al concentration favor excessive extraction resulting in the formation of large pores. Therefore, alkaline treatment of β -zeolite crystals in the second-step synthesis results in a preferential dissolution of the aluminum-poor center and the production of hollow β -zeolite crystals. ZSM-5 zeolite crystals can therefore be implanted and grown within the hollow β -zeolite crystal. The characterization result were similar to that gotten for ZSM-5/ β co-crystalline zeolite, in addition the experimental results indicates that increasing the hydrothermal treatment time will result in the formation of pure phase ZSM-5 zeolite because as treatment time increases β -zeolite converts into ZSM-5 this was tracked by FT-IR (Fourier transformed infrared) spectroscopy.

As seen earlier, the importance of hierarchical zeolite, with trimodal microporous-mesoporous-macroporous structure are also possible, as reported by Liu Haiyan *et al* [16] in their work, these property possessed by ZSM-5/Rectorite Composites zeolite allows it to increase the yield and selectivity of propylene by 2.44% and 5.35%, respectively when compared with

those of commercial ZSM-5 normally used as a catalyst in fluid catalytic cracking (FCC). The research on synthesis of ZSM-5/Rectorite was prompted by the high demand of zeolite/kaolin composites owing to the shortage in supply of high quality kaolin as starting material for the in situ synthesis leading to the research for suitable replacement for kaolin where rectorite mineral with appropriate chemical composition, prominent stability, alongside great chemical reactivity after thermal activation was discovered to be a good replacement for kaolin in the in-situ synthesis of FCC catalysts/additives. Experimental result points out that the synthesized ZSM-5/rectorite composite has much better hydrothermal stability than ZSM-5/kaolin composite synthesized using the same procedure. The material used for the synthesis are; natural rectorite mineral [containing >70%(by mass) rectorite], Sodium silicate [containing 26.3% (by mass) SiO₂ used as a supplementary silica source for synthesizing ZSM-5/rectorite composites], Silica gel [containing 25.0% (by mass) SiO₂, used as the binder for fabricating the FCC catalysts] Reagent-grade NaOH, H₂SO₄ and tetrapropylammonium bromide (TPABr) that was used as the organic template. Rectorite extrudates from calcined rectorite powder was used as the starting material, ZSM-5/rectorite composites was synthesis using the in-situ crystallization method. The synthesized ZSM-5/rectorite composites was characterized, the characterization results revealed that ZSM-5/rectorite composite constitute of both ZSM-5 and rectorite phases, with the ZSM-5 phase in-situ growing on rectorite particles as a layer of 2-3 μm in thickness, the N₂ adsorption-desorption isotherms of ZSM-5/rectorite composite indicates that it is trimodal, that is having microporous-mesoporous-macroporous structure, wherein the micropores and mesopores are attributed to the ZSM-5 crystals, and the macropores are attributed to the mother rectorite. The size of micropores in the composite is centralized at about 0.4-0.5 nm, favoring the shape-selectivity required for the cracking of linear olefins in their gasoline range, therefore boosting propylene production in FCC process [17]. A good FCC catalyst needs such an accommodating pore structure to fulfill the series reactions accruing to FCC process [18].

They include; pre-cracking of the heavier molecules in residua to the medium-size molecules in the macropores larger than 50 nm, the medium-sized molecules diffuses from macropores to mesopores of 2-50 nm where they are cracked to the middle distillate molecules lastly the middle distillate molecules diffuse from mesopores to micropores (<2 nm) where they are finally cracked into light products.

Another work carried out on hierarchical zeolite is by Jindan et al [19].

The mesopore sizes of the composite zeolite was manipulated by varying the chain length of alkyltrimethylammonium bromide (CnTAB, n = 10, 12, 14 and 16). The material used for the synthesis are HZSM-5 zeolite (SiO₂/Al₂O₃ molar ratio of 107) having an average crystal sizes of 3–4μm,

decyltrimethylammonium bromide (C10TAB), dodecyltrimethylammonium bromide (C12TAB), tetradecyltrimethylammonium bromide (C14TAB) and cetyltrimethylammonium bromide (C16TAB), n-Dodecane with 99.5 % purity was obtained.

ZSM-5/MCM-41 composite zeolites were prepared via the surfactant-directed recrystallization process via alkyltrimethylammonium bromide having various chain lengths (CnTAB, n = 10, 12, 14 and 16) as templates. 0.5 g HZSM-5 was added to 1.5 M sodium hydroxide aqueous solution (5 mL), stirring the mixture gotten for 30 min at room temperature, and adding 10 g aqueous solution of alkyltrimethylammonium (10 wt. %), with further stirring for 30 min, the mixture was then transferred into a Teflon-lined autoclave where it was hydrothermally treated for 12 h at 120°C. Allowing it to cool at room temperature, so as to adjust the pH value of the reaction mixture 2.0 M HCl was added in drops as it was stirred vigorous. The mixture was moved into the Teflon-lined autoclave where it was heated at 120°C for 24 h. recovering the product by centrifugation, it was repeatedly washed using deionized water then dried at 100°C overnight. The powder gotten was calcined at 550 °C for 6 h in order to remove the surfactant. With repeated ion-exchange using 1.0 M NH₄NO₃ solution at 90 °C for 4 h and calcinating at 550°C for 4 h, the protonated form of the samples was gotten. The samples synthesized with C10TAB, C12TAB, C14TAB and C16TAB were labeled as HZM-C10, HZM-C12, HZM-C14 and HZM-C16, respectively. The sample that was not further recrystallized after desilication with the sodium hydroxide solution was labeled as AT-ZSM-5. The resultant samples were characterized. XRD and TEM disclosed that the composites had both the characteristics of ZSM-5 and mesoporous MCM-41 alongside hexagonal symmetry. N₂-adsorption-desorption, 27Al MAS NMR, NH₃-TPD and in situ FT-IR results pointed out that the chain length of alkyltrimethylammonium bromide used is capable of affecting the sizes of the mesopores and the accessibility of acid sites. Catalytic cracking of n-dodecane over ZSM-5/MCM-41 composites was studied in the form of coatings on the inside of a tubular reactor at 550oC and 4 MPa. The conversion rate of n-dodecane grew gradually with increase in the mesopore sizes of ZSM-5/MCM-41 composites. In conclusion recrystallization in the synthesis process helped the formation of regular mesopores, where varying the chain length of alkylmethylammonium surfactants could control the resulting pore size of the composite zeolites. The recrystallization also enhanced the incorporation of Al species dissolved in the alkali treatment within the zeolite framework, preventing outrageous loss of the amount of acid sites. The presence of mesopores increased the accessibility of acid site and the diffusivity of ZSM-5/MCM-41. Therefore, ZSM-5/MCM-41 composite zeolites demonstrate higher catalytic activity in n-dodecane cracking when compared with untreated ZSM-5 and NaOH-treated ZSM-5 zeolite (without

recrystallization) and as the size of the mesopores continuously increases their catalytic activity also increases.

The work by Ping Wang et al, 2007 [20] was aimed at discovering the effect of dealumination on the catalytic property of composite zeolite. As seen early in this review, composite zeolite takes advantage of the structure of the mother zeolite phase to synthesis the other, as in the case seen above for the Growth of ZSM-5 crystals within hollow β -zeolite where the synthesis procedure took advantage of the aluminum-poor interior and aluminum-rich outer rim of β -zeolite crystals, the extraction of silicon will be favorably in the aluminum-poor bulk rather than the aluminum-rich external surface because a high framework Al concentration will hinder Si extraction, while a low Al concentration favor excessive extraction resulting in the formation of large pores where ZSM-5 zeolite were grown in, but in this case MAZ/ZSM-5 composite zeolite was synthesised taking advantage of the relative large amount of silica source that could not be used in the mother liquor of mazzite synthesis therefore it is advantageous develop a procedure to use this silica source in situ. Where in situ synthesis involves the synthesis the zeolite directly on the surface of the mother zeolite phase in this case mazzite, by using a part of the mazzite as raw material for the zeolite synthesis. First MAZ/ZSM-5 composite zeolites were synthesis in a Teflon-lined autoclave at static hydrothermal conditions using a two-step procedure.

First mazzite was synthesis by the direct chemical method.

The synthesis gel having a chemical composition of $7.7\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:16.3\text{SiO}_2:0.28(\text{TMA})_2\text{O}:343\text{H}_2\text{O}$, was autoclaved at 433 K for 48 h. secondly, the sequential product was cool to room temperature and the template ($(\text{C}_2\text{H}_5)_4\text{NBr}$ and $(\text{C}_4\text{H}_9)_4\text{NBr}$) was added, then stirred for 30 min, adjusting the pH value to a range of 10.0– 10.5 by the addition of diluted H_2SO_4 aq and crystallizing for 24 h at 433 K, the crystallized product was then filtered off, washed with deionized water and dried at 393 K for 4 h. Ion exchange was carried out on certain amount of the MAZ/ZSM-5 composite zeolite formed to give (H-MAZ/ZSM-5) and part of it was steam treated to give (DA-MAZ/ZSM-5), the resultant zeolite(DA-MAZ/ZSM-5) alongside that as from ion exchange (H-MAZ/ZSM-5) and that steam treated (MAZ/ZSM-5) were further analyzed. The XRD result indicated that all the characteristic peaks of mazzite and ZSM-5 peaks were present in the MAZ/ZSM-5, H-MAZ/ZSM-5 and DA-MAZ/ZSM-5 composite zeolite. Using SEM the morphology the composites were founded to have an irregular shape appearing together with two phase particles grown together showing that when the zeolites were crystallized at least one part of these two zeolites were “joined” together to make the composite. BET surface area and pore volume of the composite zeolite can be markedly changed after ion exchange and steam treatment, leading to an obvious increases in pore volume and BET surface area compared with

parent MAZ/ZSM-5, further catalytic analysis of the zeolite composite revealed that by mild dealumination treatment, the properties of the MAZ/ZSM-5 composite can be markedly changed, leading to the creation of secondary mesopore network also steaming created secondary mesopore network.

The functionalization of zeolites external surface of can be improved via different method such as acid leaching, steaming and element surface modification induce mesopores and obtain a reasonable acid distribution [21-23]. Another method that can be use, is the growth of a continuous shell over core crystals but using this method the importance of chemical compatibility and structure similarity of shell and core has to be put into consideration alongside the merging the crystallization conditions targeted at producing a shell around single crystal. All the above synthesis discussed has focused on synthesizing composite zeolite as a result of intimate co-crystallization of zeolite materials with hybrid crystals and epitaxial growth phenomenon with specific selective orientation on a diversity of crystal faces which could be obtained in a one-step synthesis technique.

Another work on composite zeolite follows the synthesis based on intimate co-crystallization of zeolite materials with hybrid crystals and epitaxial growth phenomenon with specific selective orientation on a diversity of crystal faces in a one-step synthesis technique which was carried out by a two-step crystallization process involving the in situ crystallization of NaY on kaolin where kaolin is used as the starting material and MCM-41 was then overgrown on the surface of kaolin/NaY composites. Characterized the synthesized composite using XRD, SEM, differential thermal analyses (DTA), N_2 adsorption NMR, TG, and IR spectra. XRD analyses indicated that the kaolin/NaY/MCM-41 composites obtained possess the typical characteristics of well-ordered mesoporous MCM-41 and NaY zeolite. N_2 adsorption showed that a stepwise-distributed pore structure exists in the composites. Both NMR and IR spectra proposed that the composite is different from the mechanical mixture of the three phase. Compared kaolin/NaY/MCM-41 composites with its mechanical mixture, the composite was seen to possess higher hydrothermal stability alongside more Brønsted and Lewis acid sites., since their external surface active sites are low in concentration, their role in catalytic reactions is not negligible because they set restrictions for reactants to reach active sites in the microspores [24]. Another two step crystallization process used in synthesis of composite zeolite is that by Chi He *et al* [25] where it was revealed that the amount of strong acid sites increases as the Si/Al molar ratio decreases, while that of weak acid sites is almost unchanged. The synthesis was carried out by assemblage of cetyltrimethylammonium bromide (CTAB) in a preformed ZSM-5 colloidal gel. The micro/mesoporous composite materials were hydrothermally synthesized, with the ZSM-5 primary unit, the precursor zeolite colloidal suspension was prepared via the mixing of 21.1 g of H_2O , 7.1 g of 20

wt.% tetrapropylammonium hydroxide (TPAOH), 10.6 g of tetraethyl orthosilicate (TEOS), and different amounts of aluminium isopropoxide and stirring for 2 h, allowing an aging time of 4h for the mixture the at 100 °C and cooling down to room temperature, the resulting ZSM-5 zeolite suspension gotten was added with a CTAB solution containing a stoichiometrical amount of NaOH to a final gel molar composition of TEOS:OH:Al:CTAB:H₂O= 1:0.5:x:0.12:118, was stirred for 2 h at room temperature, the prepared gel was moved into an autoclave where it was been heated at 150 °C for 8 h, after filtrating, and drying at 60 °C, calcination was done at 550 °C for 6 h. subsequently, the calcined sample underwent ion exchange with 0.1M NH₄NO₃ solution (two exchange cycles) for 24 h at room temperature then calcinated for 4h at 500 °C to produce the protonated form. Pd was loaded by impregnating the porous support with a PdCl₂ aqueous solution and drying at 100 °C overnight, then calcinating at 500 °C for 4 h and reduced in a pure H₂ stream (30 ml/min) for 2 h at 480 °C. The characterization results of Pd/ZSM-5/MCM-48 showed that ZSM-5 seeds are present in the framework with its content gradually increasing as the Si/Al molar ratio increases, and Al atoms prefer the tetrahedral coordination in composite products, amount of strong acid sites increases as the Si/Al molar ratio decreases. The catalytic test of the resultant composite when compared with Pd/ZSM-5 and Pd/MCM-48 pointed out that the Pd-loaded ZSM-5/MCM-48 composite catalysts is much higher than that of Pd/ZSM-5 and Pd/MCM-48, and that they are all active and stable in the total oxidation of benzene.

CONCLUSION

As seen from all the cases considered, zeolites can be modified to suit any application by either incorporating a metal or non-metal in a zeolites phase by means of impregnation, intimate co-crystallization of zeolite materials or growth of a known zeolite phase on another forming the composite. Composite zeolite are very essential because they help in improving adsorptive as well as catalytic performance and increase the range of functionalities of zeolites.

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