CHAPTER I
INTRODUCTION

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I.1. Porous materials

Porous materials have been intensively studied with regard to technical applications as catalysts and catalyst supports. According to the IUPAC definition, porous materials are divided into three classes; microporous (pore size < 2nm), mesoporous (2–50nm), and macroporous (>50nm) materials.[1] In addition, also the term "nanoporous" is increasingly being used. However, it is not clearly defined and loosely refers to pores in the nanometer size range.

Among the family of microporous materials, the best known members are zeolites which have a narrow and uniform micropore size distribution due to their crystallographically defined pore system.

In recent years, environmental and economic considerations have raised strong interest to redesign commercially important processes so that the use of harmful substances and the generation of toxic waste could be avoided. In this respect, there is no doubt that heterogeneous catalysis can play a key role in the development of environmentally benign processes in petroleum chemistry and in the production of chemicals, for instance by substitution of liquid acid catalysts by solid materials. Especially zeolites have attracted strong attention as such acids, but also as base and redox catalysts. However, zeolites present severe limitations when large reactant molecules are involved, especially in liquid-phase systems as is frequently the case in the synthesis of fine chemicals, due to the fact that mass transfer limitations are very severe for microporous solids. The access of the reactants to their internal surface is limited to molecules with diameters below 10 Å.

Attempts to improve the diffusion of reactants to the catalytic sites have so far focused on increasing the zeolite pore sizes,[2] on decreasing zeolite crystal size,[3] or on providing an additional mesopore system within the microporous crystals.[4, 5]

In order to preserve the remarkable catalytic properties of the zeolites while expanding their use to process bulkier molecules, new synthesis routes have been undertaken to increase their pore diameter. The strategy followed was based on the observation that most of the organic templates used to synthesize zeolites affect the gel chemistry and act as void fillers in the growing porous solid. Thus it was a logical move to increase the size of the organic template hoping that it will result in larger voids in the synthesized material. This approach did not lead to larger pore zeolites, but was responsible for the formation of ultra large pore molecular sieves when using Al and P or Ga and P as framework elements.[2, 6-15]

Only recently a 14 member ring (MR) unidirectional zeolite (UTD-1) could be synthesized using Co organometallic complex as the template.[16, 17] However, when the zeolite and zeotypes with the largest known diameters are considered in the context of their possible uses as catalysts the following can be said: cacoxenite,[18] which is a naturally occurring mineral with a 15 Å pore system, is thermally unstable and thus cannot be used as catalyst. In the case of cloverite,[12] while it has potentially large pores, the unusual shape of the pore openings which are altered due to protruding hydroxyl groups limits the diffusion of large molecules.

Likewise, in VPI-5 [10] stacking disorder or deformation of some of the 18 member ring during dehydration results in a decrease in the pore size from 12 to about 8 Å. Furthermore, this structure does not contain acid or redox groups which may serve as catalytic centers and isomorphous SAPO or TAPO structures should be prepared.

Finally, in the case of UTD-1 the fact that has to be synthesized with an organometallic complex which has to be destroyed by calcination can limit the actual use of the material. Nevertheless it may be of direct interest for preparation of zeolite metal supported catalysts.

I.2. Ordered mesoporous molecular sieves

Mesoporous molecular sieves have attracted much attention owing to their potential use as versatile catalysts and adsorbents for bulky molecules.[19, 20] These materials contain a regular arrangement of uniform channels with diameters between 2 and 10 nm, high specific surface area and high specific pore volume. They are potentially promising candidates for use in catalysts,[21-28] adsorbents,[29-32] sensors,[33] and hosts.[34, 35]

The first synthesis of an ordered mesoporous material was described in the patent literature in 1969. However, due to a lack of analysis, the remarkable features of this product were not recognized.[36, 37]

In 1990, Kuroda and coworkers first reported the preparation of mesoporous silica with uniform pore size distribution from the layered polysilicate kanemite,[38, 39] which serves as a silica source, the pathway leading to the ordered mesoporous material is thought to proceed via surfactant intercalation into the silicate sheets, warping of the sheets and transformation to the hexagonally packed material. Modifying and optimizing the reaction conditions yielded highly ordered mesoporous silicates and aluminosilicates as well.[39, 40] The obtained materials are designated as FSM-n, Folded Sheet Mesoporous Materials-n, here n is the number of carbon atoms in the surfactant alkyl chain used to synthesize the material.

In 1992, a significant breakthrough in the mesoporous materials research has come when mobil scientists disclosed the M41S family of materials, which stands for Mobil Composition of Matter No. 41(MCM-41), shows a highly ordered hexagonal array of unidimensional pores, high specific surface areas and specific pore volumes, including MCM-41 (with a hexagonal arrangement of the mesopores, space group p6mm),[19,41] MCM-48 (with a cubic arrangement of the mesopores, space group Ia3d),[42] MCM-50 (with a laminar structure, space group p2).[43]

Fig.1. Structures of mesoporous M41S materials: a) MCM- 41(2D hexagonal, space group p6mm), b) MCM-48 (cubic, space group Ia3d) and c) MCM-50 (lamellar, space group P2).

At approximately the same time, an alternative, but less versatile approach to mesoporous materials was described by Yanagisawa et al.[38]

These pioneering findings were followed by various kinds of mesoporous materials. For example, Hexagonal Mesoporous Silica (HMS) prepared using neutral amine as template possesses slightly disordered hexagonal structure and thicker walls, superior thermal stability upon calcination in air, and a smaller crystallite size, which affords complementary textural mesoporosity for improved access to the framework-confined mesoporous [44] Michigan State University (MSU-1) synthesized by using polyethylene oxide (PEO) as a structure directing agent also has a disordered channel structure.[45] This material possesses large wall thickness and small particle size with considerable textural mesoporosity due to pores formed between the relatively small particles.

Meso Cellular Form (MCF) materials can be prepared by using triblock-copolymers stabilized oil in water to result in aerogel-like structure, which offers the benefits as catalyst supports and separation media.[46]

As widely used materials, highly ordered large pore mesoporous silica Santa Barbara Amorphous-15 (SBA-15) with thicker pore walls and two dimensional hexagonal structure, by using amphiphilic triblock-copolymer of poly(ethylene oxide) and poly(propylene oxide) (Pluronic P123) as the structure directing reagent in highly acidic media.[47,48] The pore diameters of the SBA materials are well tunable in the range of 5~30 nm and these materials exhibit higher hydrothermal stability as compared to that of other mesoporous materials.

I.3. Behavior of surfactant molecules in an aqueous solution

In a simple binary system of water-surfactant, surfactant molecules manifest themselves as very active components with variable structures in accordance with increasing concentrations, as schematically shown in Fig. 2.
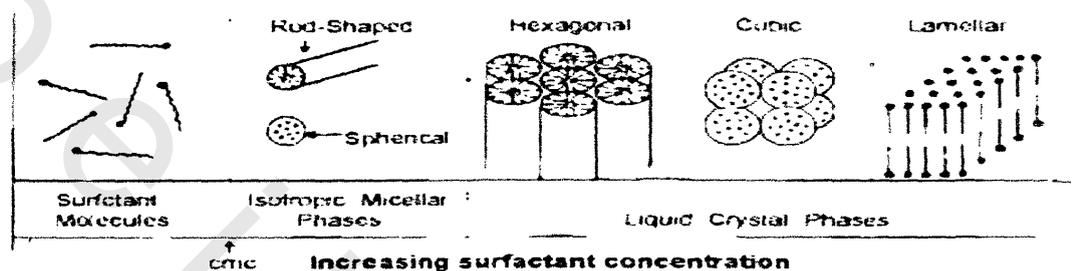

Fig.2. Phase sequence of surfactant – water binary system [49, 50]

At low concentrations, they energetically exist as monomolecules. With increasing concentration, surfactant molecules aggregate together to form micelles in order to decrease the system entropy.

The initial concentration threshold at which monatomic molecules aggregate to form isotropic micellesis called cmc (critical micellization concentration). As the concentration process continues, hexagonal close packed arrays appear, producing the hexagonal phases.[50]

The next step in the process is the coalescence of the adjacent, mutually parallel cylinders to produce the lamellar phase. In some cases, the cubic phase also appears prior to the lamellar phase. The cubic phase is generally believed to consist of complex, interwoven networks of rod-shaped aggregates.[51]

According to Myers,[49] the particular phase present in a surfactant aqueous solution at a given concentration depends not only on the concentrations but also on the nature of itself (the length of the hydrophobic carbon chain, hydrophilic head group, and counterion) and the environmental parameters (pH, temperature, the ionic strength, and other additives).

5

One of the most useful groups of surfactants is the triblock co-polymers consisting of Poly (ethylene oxide) $_x$-poly- (propylene oxide) $_y$-poly (ethylene oxide) $_x$, (PEO) $_x$(PPO) $_y$ - (PEO) $_x$ (trade name: Pluronics) which show the ability to form liquid‐crystal structures.

I.4. Synthesis of ordered mesoporous molecular sieves

Depending on the synthesis conditions, the silica source or the type of surfactant used, many other mesoporous materials can be synthesized following the co-operative assembly pathway.[52-54] In addition to the co-operative pathways, also the true liquid crystal templating pathway [55] and nanocasting using already formed ordered mesoporous materials as hard templates [56, 57] have been developed over the last ten years.

From the viewpoint of the template used for synthesis, the interaction of inorganic species and organic template molecule, and according to the suggestion of Huo et al.[53, 54] These interactions are classified as follows:

If the reaction takes place under basic conditions (whereby the silica species are present as anions) and cationic quaternary ammonium surfactants are used as the Structure-Directing Agent (SDA), the synthetic pathway is termed S^+I^- (Fig.3a; S: surfactant; I: inorganic species).The preparation can also take place under acidic Conditions (Below the isoelectric point of the $Si\,OH$ bearing inorganic species; pH≈2), whereby the silica species are positively charged.

To produce an interaction with the cationic surfactant, it is necessary to add a mediator ion X^- (usually a halide) ($S^+X^-I^+$; pathway; Fig.3b). Conversely, when negatively charged surfactants (e.g., long-chain alkyl phosphates) are used as the SDA, it is possible to work in basic media, whereby again a mediator ion M^+ must be added to ensure interaction between the equally negatively charged silica species ($S^-M^+I^-$; pathway ;Fig.3c); a mediator ion is not required in acidic media (S^-I^+; pathway ;Fig.3d).

Thus, the dominating Interactions in pathways (a–d) are of an electrostatic nature. Moreover, it is still possible for the attractive interactions to be mediated through hydrogen bonds. This is the case when nonionic surfactants are used (e.g., S^0: a long-chained amine; N^0: polyethylene oxide), whereby uncharged silica species (S^0I^0; pathway; Fig.3e) or ion pairs ($S^0 (XI)^0$; pathway; Fig.3f) can be present.
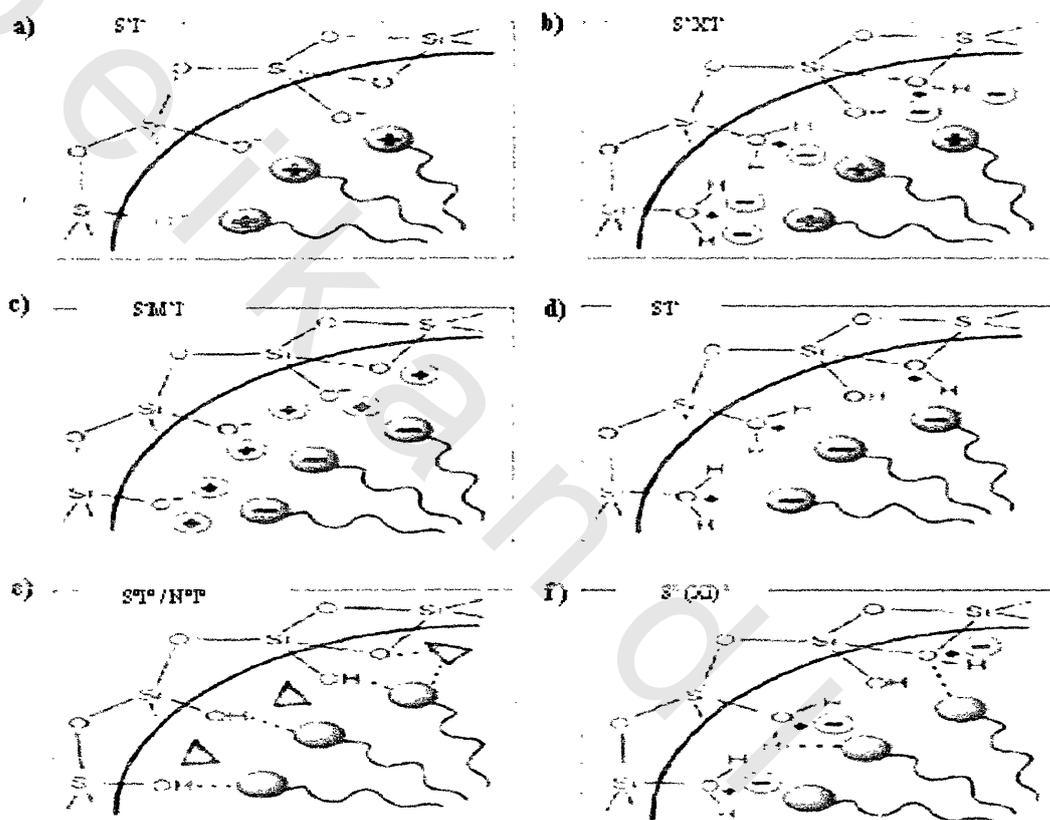

Fig.3. Interaction between the inorganic species and the head group of the surfactant

I.5. Control of local environment and morphology

Recently, the thermal, hydrothermal, and mechanical stabilities of various mesoporous silicas, e.g. MCM-41, MCM-48, HMS, FSM-16, KIT-1, PCH (porous clay hetero structure) [58] and SBA-15, have been studied by Galarneau et al.,[59] Cassiers et al. [60] and Igarashiet al.[61]

It was discovered that the thermal stability strongly depends on the wall thickness of the mesoporous materials and the silica precursor used in the synthesis.

Hydrothermal stability is influenced by the wall thickness as well, but the degree of silica polymerization has also a very strong influence on hydrothermal stability.

Mechanical stability, on the other hand, is only little influenced by the nature of the mesoporous materials and is usually sufficient for application of ordered mesoporous solids in most catalytic applications.

Since hydrothermal stability is essential for most possible applications of mesoporous materials in catalysis, several approaches were developed to improve this property. The strategies that have been investigated include the addition of salts during the hydrothermal synthesis,[62] modification of the surface by silylation [63] or post-synthesis grafting of inorganic compounds to increase the wall thickness or to chemically stabilize the wall surface.[64]

Among the wide variety of application areas, our interest has focused on the preparation of heterogeneous catalysts supported on ordered mesoporous materials. In such a system, the confinement of nanoparticles in the mesochannels of mesoporous silicas aids in stabilizing the highly dispersed metals and oxides in uniform porous matrixes.[26, 27, 65] Furthermore, ordered mesoporous materials have a more uniform pore structure and a larger surface area than conventional industrial catalyst supports, and their tunable mesoporosity may reduce the extent of deactivation due to coke formation and plugging phenomenon that occurs in the micropores, which blocks pores, leading to limitations in the mass-transfer of reactants and products.[66]

Therefore, ordered mesoporous materials have the potential for use as high performance catalyst supports. Among the diverse ordered mesostructured family, Because of its relatively high mechanical, thermal, and hydrothermal stabilities with a well-defined pore structure and uniform pore sizes of cylindrical shape,[67, 60] we have concluded that SBA-15 is one of the most promising catalyst supports for practical industrial applications in the field of heterogeneous catalysis.

For the above reasons, SBA-15 was used as a support for the heterogeneous catalysts in this study.

I.6. Mesoporous Santa Barbara Amorphous-15 (SBA-15) molecular sieves

In 1998, Zhao et al.[47,48] synthesized mesostructured silica SBA-15 using amphiphillic triblock copolymers to direct the organization of silica species under strong acid conditions.

This material is a well ordered hexagonal mesoporous silica structure with uniform pore size and considerably thicker pore walls as compared with MCM-41 and, thus, exhibits significantly higher hydrothermal stability than the latter material.

The mesoporous diameter of SBA-15 depends on the synthetic conditions: increasing the gel aging temperature leads to a larger pore diameter. [47, 68]

One interesting feature of SBA-15 is the microporosity which is present in its mesopore wall, by which the micropores connect neighboring mesopores. By careful investigation of XRD and the modeling of the diffraction patterns, Impèror-Clerc et al. found that the walls had a "microporous corona" region resulting from partial embedding of the PEO part of the surfactant in the mesopore wall. [69] The authors suggested that this corona is converted to micropores upon calcination.

I.7. Mechanism of formation of SBA-15

In 2008, Zholobenko et al.[70] confirmed that the formation of SBA-15 proceeds according to the cooperative self-assembly mechanism. They identified three major stages in the synthesis of SBA-15 and established the structure of relevant intermediates as summarized in Fig. 4.
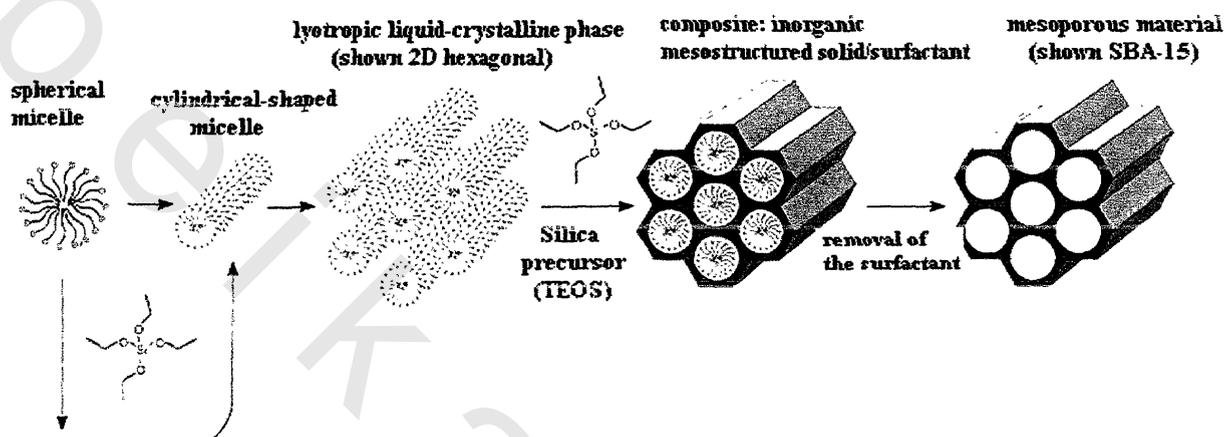

Fig.4. The synthesis stages of the formation of mesoporous SBA-15 [71]

Zholobenko et al. used in situ SANS (Small Angle Neutron Scattering) which enabled the identification of the initial stages of SBA-15 synthesis. The three major stages can be stated as follow:

1- Only spherical micelles of P123 block copolymer are present in the synthesis mixture during the first stage.

2- The second stage of the synthesis, the formation of hybrid organic–inorganic micelles was observed accompanied with the transformation from spherical to cylindrical micelles, which takes place before the precipitation of the ordered SBA-15 material.

The second stage can be explained by the synthesis mechanism of SBA-15 proposed by Zhao et al.[48] According to this mechanism, the formation of hexagonal mesophase under highly acidic conditions occurs through the $S^0H^+X^-I^+$ pathway (nonionic polymeric surfactant (S^+), halogen anions (X^-), and the protonated inorganic SiO_2 Species (I^+)). At very high pH, the alkylene oxide groups of the surfactant are solubilized and the hydronium ions are associated with the alkylene oxygen atoms. Since the point of zero net charge of silica is at pH~ 2, the silica species are positively charged

10

by proton abstraction at low pH. The charge-associated alkylene oxide units and the cationic silica species are assembled together by a combination of electrostatic, hydrogen bonding, and van der Waals interactions REO_{m-y} [(EO).H_3O^+]y...yX^-...I^+, which can be designated as (S^0H^+)(XI^+).

3- During the third stage, these micelles begin to aggregate into a two-dimensional hexagonal structure, confirming that the precipitation takes place as the result of self-assembly of the hybrid cylindrical micelles into the two dimensional hexagonal structure of SBA-15.

Initially, the cylinders are only weakly linked via their coronas in the hexagonal matrix. As the synthesis proceeds, the voids between the cylinders are increasingly filled with the silicate species which undergo condensation reactions resulting in cross-linking and covalent bonding between coronas of the cylindrical micelles. The condensation of the silicate species continues for the duration of the experiment, ~20 h, at 40 °C. At this stage, subsequent exposure of the synthesis mixture to higher temperatures, typically 80–100 °C under hydrothermal conditions and about 500 °C during calcination, leads to further condensation and densification of the structure, accompanied with a decrease in the unit cell parameter and an increase in the pore size, resulting in the formation of highly ordered and thermally stable SBA-15 mesoporous phase Fig.5.
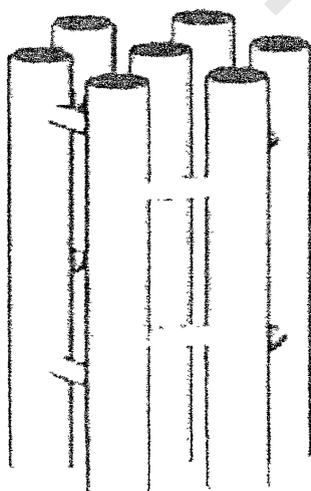

Fig.5. SBA-15 [72]

The pure siliceous SBA-15 consisting of pure-silica frameworks have electrically neutral framework and consequently no Brønsted acidity. Therefore are of limited use for various catalytic applications because of the lack of acid sites and ion exchange capacity.[73]

I.8.The incorporation of aluminum into SBA-15

The incorporation of aluminum within the silica framework of mesoporous materials has been implemented in order to increase their acidity, ion-exchange capacity, and catalytic activity.[73]

It is very difficult to prepare SBA-15 containing heteroatoms in the framework because of the strong acidic synthesis conditions. Recently, many efforts have been made to incorporate of Al, Ti and V into the framework of SBA-15, by post-synthesis grafting procedures [74-76] and direct synthesis.[77, 78]

During materials preparation via postsynthetic methods often metal oxides are formed in the channels or on the external surface. Metal oxides formed in the mesopores will block the pores partially or fully, thereby reducing surface area, pore volume, and pore diameter.[79]

Several post-synthesis methods where aluminum was grafted onto the mesoporous wall with various aluminum sources have been developed without the mesoporous structure seriously destroyed.[74, 80] Which consists of reacting the silanol groups on the wall surfaces with aluminum chloride, aluminum isopropoxide or $NH_4/3AlF_6$ in nonaqeous solution and then followed by calcination, has been proposed.[80-86]

The post synthesis procedure needs two steps (reaction and calcination) and is not easy to ensure the incorporation of the active species into the channels of mesoporous materials without forming relatively large aggregates which can block the pore openings and play a negative role in catalysis.[87]

A different strategy is the transformation of amorphous SBA-15 walls into crystalline aluminosilicates [88, 89] even though the materials formed are good cracking catalysts, the synthesis procedure is somewhat tedious and requires two steps. Therefore, it is still a challenge to find a one-step route to SBA-15 materials with high Al

content in order to increase the acidity without changing its structural order or increasing the complexity of the synthesis.

To solve the problems and simplify the preparation procedures, direct-synthesis of Al substituted SBA-15 materials was developed via the hydrothermal treatment.

Yue et al.[77] reported the direct synthesis of AlSBA-15 by using aluminum tri-tert-butoxide as aluminum precursor and found that catalytic activity of AlSBA-15 in cumene cracking is higher as compared to AlMCM-41, but the product contains extra framework aluminum species and post-synthetic method is necessary to remove the extra framework octahedral aluminum.

In 2004, Vinu et al.[90] reported the direct incorporation of high amount of Al in the SBA-15 framework containing exclusively tetrahedrally aluminum by simply adjusting the molar water to hydrochloric acid ratio of the synthesis medium at 276 and also studied the influence of aluminum sources on the extent of metal incorporation and found that Al isoprpoxide was the preferred Al source. They also Found that pore diameter of the AlSBA-15 materials can easily be controlled by changing the synthesis temperature

At the same time, Li et al.[91] directly fabricated Al-SBA-15 materials via hydrolysis-controlled approach using tetramethylothosilicate (TMOS) as silica precursor

In 2007, Li and his coworkers[92] prepared extremely hydrothermal stable Al-SBA-15 material under the assistance of sodium chloride

In 2008, Wang and Liu[93] developed a new direct simple efficient and energy saving synthesis route of Al-SBA-15 materials by using Evaporation- Induced Self Assembly (EISA) method where no mineral acid and hydrothermal treatment were used. Using tetraethylothosilicate (TEOS) and aluminum chloride as silicon and aluminum precursors, respectively.

I.9. Mechanism of formation of AlSBA-15

The incorporation of Al into SBA-15 under retained structural order with increasing n_{H2O}/n_{HCl} ratio can be explained by the synthesis mechanism proposed by Vinu et al. [90]

As already mentioned a high acidic medium is necessary for the formation of the hexagonal mesophase SBA-15 but prohibits the introduction of aluminum due to the high solubility of the Al isoprpoxide precursor at high pH. This can be explained by the Following equations:

$$Al\,(C_3H_7O)_{3(S)} + 3H^+_{(aq)} \longleftrightarrow Al^{3+}_{(aq)} + 3C_3H_7OH_{(aq)} \quad (1)$$

$$Al^{3+} + 2H_2O \longrightarrow Al\,(OH)^{2+} + 2H^+ \quad (2)$$

Vinu et al. optimized the pH of the synthesis medium by adjusting the n_{H2O}/n_{HCl} ratio at 276. By using this ratio once the surfactant and silica species are protonated, the cationic silica species undergo partial condensation and form mesostructure through the counteranion (X⁻) with the cationic surfactant species; as a result, pH of the synthesis medium was around 2.1, which is above the zero net charge of silica. If the pH of the synthesis medium rises above the zero net charge of silica, the silica species are negatively charged which enhances the interaction with the Al (OH)$^{2+}$ species. With decreasing H$^+$ concentration in the synthesis gel, the concentration of aluminum hydroxyl species increases (eq 2). Hence, the partially condensed silica species are able to form Al-O-Si bond with Al (OH)$^{2+}$ species at high pH. Moreover, the structural order of the materials is maintained when formed at a pH of ca. 2.
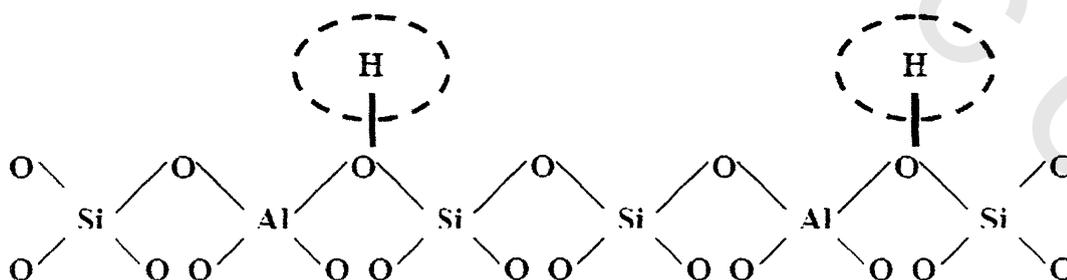

Fig.6. Brønsted acid form of AlSBA-15

I.10. Paraffins hydroconversions

The hydroconversion of n-paraffins is one of important processes in petroleum industry for obtaining good quality of middle distillates.[94, 95] These components, especially their long-chain forms, have bad effect on some properties of oil products, and therefore should be removed. One conventional method for removal is isomerization of n-paraffins to isoparaffins. The isomerization process usually takes place in the presence of hydrogen, and in this case it is referred to as hydroisomerization.[96]

Hydroisomerization of C_4–C_7 hydrocarbons apply in the production of gasoline with a high octane number.[97–100] The cuts such as light strength run (LSR) and light naphtha consist of this kind of n-paraffins; with hydroisomerization of them, one obtains high octane number gasoline.[100] Isomerization of C_7–C_{15} paraffins applies to production of diesel fuel with high cetane number and improved cold flow properties, such as viscosity, pour point and freezing point.[98, 101, 102] n-Paraffins Heavier than C_{15} make up greater than 80 wt % of the material with the name wax.[103]
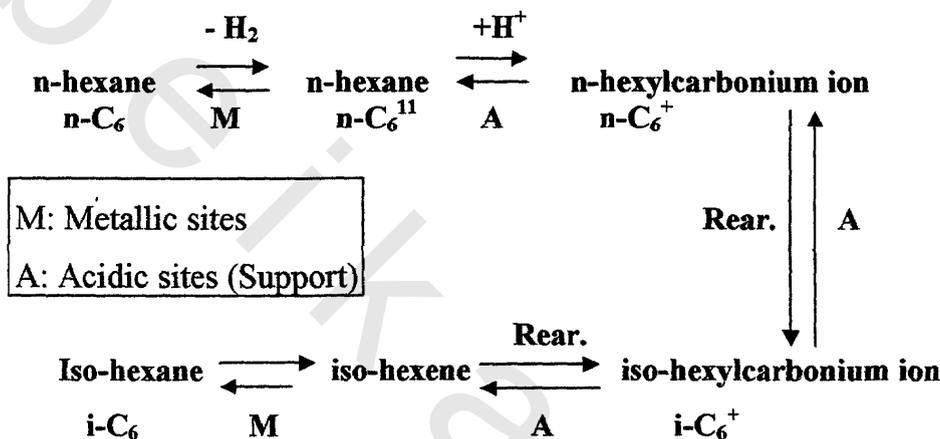
Normally, lube and middle distillate cuts have large amounts of wax. Wax increases the freezing and the pour points of these cuts, because of its solid form at ambient temperature. The commercial products such as fuel jet and lubricant oil produced from these cuts should have low freezing and pour points. To produce these products with high quality, one should isomerizes the wax to isoparaffins.[103–105]

The hydroisomerization reaction is always accompanied by a hydrocracking reaction that lowers more or less the yield of that the isomerized feed molecules.
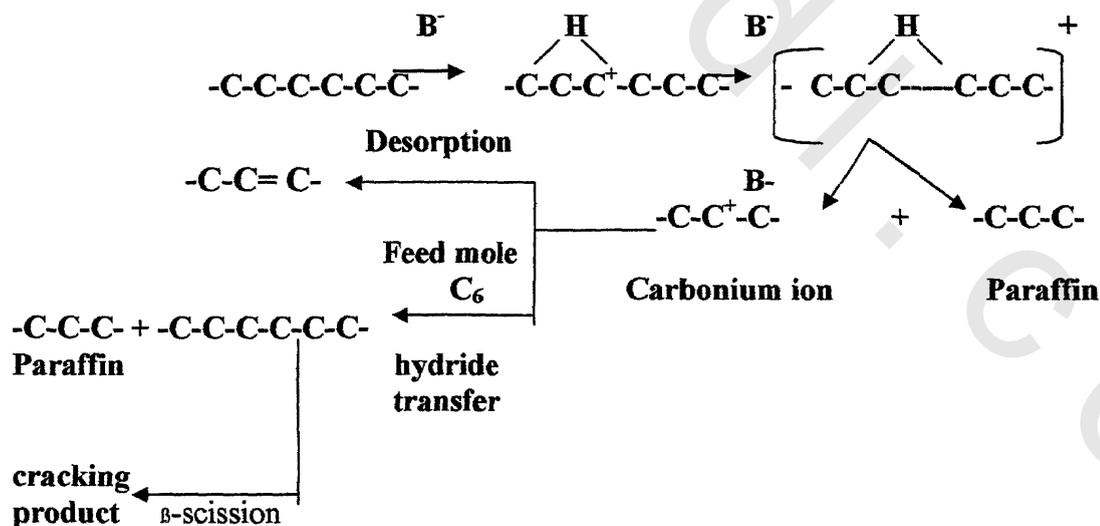
It is well established that isomerization of n-paraffins occurs first and cracking is a consecutive reaction, which is favored for multibranched alkanes. Monobranched paraffins are less susceptible to cracking than multibranched paraffins. Thus, in order to decrease cracking reactions one must limit multibranching.[106–108]

The hydroconversion process is usually carried out using a metal/acid bifunctional catalyst, over which the alkanes are dehydrogenated–hydrogenated on metallic sites and then isomerized or cracked on the acid sites through classical or nonclassical ion carbenium mechanism.[109–111] The hydroisomerization and hydrocracking mechanism can be illustrated as follows:

-The hydroisomerization mechanism:

$$
\text{n-hexane} \underset{M}{\overset{-H_2}{\rightleftharpoons}} \text{n-hexane} \underset{A}{\overset{+H^+}{\rightleftharpoons}} \text{n-hexylcarbonium ion}
$$

n-C_6 M   n-C_6^{11} A   n-C_6^+

| M: Metallic sites |
| A: Acidic sites (Support) |

Rear. │ A

Rear.

Iso-hexane $\rightleftharpoons$ iso-hexene $\overset{Rear.}{\rightleftharpoons}$ iso-hexylcarbonium ion

i-C_6 M   A   i-C_6^+

-The hydrocarcking mechanism:

$$-C-C-C-C-C-C- \overset{B^-}{\underset{H}{\longrightarrow}} -C-C-C^+-C-C-C- \overset{B^-}{\underset{H}{\longrightarrow}} [-C-C-C\text{---}C-C-C-]^+$$

Desorption

-C-C= C- ⟵

B-
-C-C⁺-C-   +   -C-C-C-

Feed mole C_6

Carbonium ion   Paraffin

-C-C-C- + -C-C-C-C-C-C-
Paraffin   hydride transfer

cracking product   ß-scission

Thus, the balance between metal and acid sites is critical in determining the activity, stability and product selectivity of these catalysts.[112–114]

In the past few decades, many studies have been performed on the catalytic performance of metal-loaded zeolite bifunctional catalysts. It was generally considered that microporous zeolite-based catalyst have advantages in producing lower coking and higher hydrocracking activity with respect to the amorphous catalysts.[115]

Metal oxides-emerged mesoporous silica materials have been reported with various pore structures, making them important materials with considerable and versatile properties.[116]

I.11. Catalytic application of metal supported SBA-15 and AlSBA-15

The NiMo/AlSBA-15 sulfide catalyst with higher Mo loading (17 wt %) showed HDN and HDS activities similar to the conventional NiMo/γ-Al$_2$O$_3$ sulfide catalyst with real feed stock.[117]

The hydroisomerization of n-dodecane had been investigated over bifunctional catalyst Pt/Al-SBA-15. The results showed that the largest isomers yield of n-dodecane reaches 51% for Pt/Al-SBA-15 with Si/Al ratio of 8, at the same ratio, the largest isomers yield for Pt/Al-SBA-15 is higher than that for Pt/AlMCM-41suggesting that a proper balance between acid and hydrogenating functions was found for Pt/Al-SBA-15 catalyst.[118]

The activity in gasoline production from waste palm oil had been examined over Aluminum –containing SBA-15 mesoporous materials prepared via direct synthesis and via post-synthesis method. Both catalysts gave comparable activity but the one prepared via post-synthesis method exhibited higher activity and yield of gasoline fraction as compared to the one prepared by direct synthesis. The authors attributed that behavior to the better thermal stability of Al-SBA-15 catalyst prepared via post synthesis method.[119]

Hydrocarcking of petroleum asphaltene with Fe and Ni catalysts loaded on SBA-15 had been investigated concluding that the use of the 10% Ni catalyst instead of the 10% Fe catalyst provided a slight decrease in asphaltene conversion but a remarkable improvement in selectivity to maltene, which means the larger the effectiveness of the Ni for selective conversion of asphaltene to maltene.[120]

The dehydrogenation of propane (DHP) had been investigated over Pt-SBA-15 catalysts. The results revealed that Pt particle size was an important parameter to be taken into account while designing a rational catalyst for DHP as Pt particle size not only influenced the reaction activity but also played a crucial role in determining selectivity as evidenced by cooking.[121]

Hydrogenation of aromatic compounds, such as naphthalene or tetraline was examined over Ni/SBA-15 catalyst prepared using Deposition – Precipitation method. The results showed that Ni/SBA-15 was three times more active than Ni/MCM-41 attributing the difference in activity to the smaller size of Ni particles in the Ni/SBA-15 compared to the size of Ni reported for the Ni/MCM-41 catalyst.[122]

The selective catalytic reduction of NO by propene had been investigated over Pt/SBA-15 and Pt/AlSBA-15 catalysts in the presence of oxygen. The results showed that the Pt/AlSBA-15 catalysts had better activity than Pt/SBA-15, attributing the increased NO conversion to the presence of certain degree of support acidity of Pt/AlSBA-15.[123]

The hydrodesulphurization (HDS) activity had been investigated in many papers over NiMo/SBA-15 and NiMo/AlSBA-15 catalysts. The results revealed that AlSBA-15 seem to be more suited for the preparation of new catalysts for deep HDS than traditionally used microporous crystalline zeolites which attributed to the weaker Brønsted acid sites strength of the AlSBA-15 supports. Also, the support Si/Al molar ratio affected the HDS activity and selectivity of the catalysts. SBA-15 and Al-SBA-15 supported catalysts showed similar activities for HDS.[124-126]

The hydrodesulphurization (HDS) activity over Pt/SBA-15 and Pt/AlSBA-15 catalysts had been investigated. The HDS activity of Pt/AlSBA-15 catalyst was higher than that of commercial CoMo/ γ-Al$_2$O$_3$ HDS catalyst, whereas the activity of Pt/SBA-15 was lower than that of pt/ γ-Al$_2$O$_3$ at equal Pt loading due to the higher acidity of γ-Al$_2$O$_3$.[127, 128]

18