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Adsorption Equilibria of Xylene Isomers in a Mobil Composition of Matter

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To my father

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To the spirit of my pure mother

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List of Abbreviations:

Symbols

B	Langmuir constant or adsorption affinity constant, Pa ⁻¹
b₀	frequency factor of the affinity constant, Pa ⁻¹
CTAB	CetylTrimethyl Ammonium Bromid
DMT	Dimethyl Terephthalate
DSL	Dual-site Langmuir
EB	Ethylbenzene
HPLC	high performance liquid chromatography
IUPAC	International Union of Pure and Applied Chemistry
IR	Infra Red
MCM	Mobil Composition of Matter
M41S	MCM Family
M-X	Meta-xylene
N	total number of measurements, dimensionless
O-X	Ortho-xylene
P	Partial pressure (bar)
PBT	Polybutene of terephthalate
PET	Polyethylene terephthalate
PPT	Polypropylene terephthalate
PTA	Purified terephthalic acid
P-X	Para-xylene
Q	amount adsorbed, p is the pressure of sorbate, g/100gads
q_s	saturation capacity of each type of sites, respectively, g/100gads
R	ideal gas constant, Pa m ³ mol ⁻¹ K
SBU	Secondary building unit
SMB	Simulated moving bed
T	temperature, K
TMAOH	Tetramethylammonium hydroxide

Gregorian Letters

ΔH	heat of adsorption, kJ/mol
ΔH_{st}	isosteric heat of sorption, kJ/mol
H	number of active sites of adsorption, dimensionless
Θ	Adsorbed fraction (g/100gads)

Lower Indices

I	Component or counter
J	Component or counter
K	Component or counter
S	Saturation

Higher Indices

C	Relative to wide channels of the MCM-41
J	Relative to narrow MCM-41 channels

ABSTRACT

Separation of molecular isomers, which have similar physical properties, is hardly achieved with conventional separation methods based on phase equilibria. However, using selective inclusion of target molecules into mobil composition of matter allows molecular isomers to be effectively separated from one another.

Single and multicomponent adsorption equilibria of xylene isomers: o-xylene (o-x), m-xylene (m-x), p-xylene (p-x) and ethylbenzene (eb) will investigate on the three dimensional microporous MCM-41 in the range of temperatures between 398 and 448 K and partial pressures up to 0.1 bar. The Dual-Site Langmuir model (DSL) will be used for the interpretation and correlation of the experimental data.

The aim of the present work is (i) – Separation of the mixture of xylene isomers and ethyl benzene by adsorption equilibria (ii) Investigate the use of mesoporous silica material such as MCM-41 as an adsorbent due to their low cost and also for their big stability.

KEYWORDS: Adsorption equilibria, MCM-41, Xylene isomers.

I. Background and objectives

I.1 Background

The most widely recognized benzene homologs with the general formula C_8H_{10} are mixed xylenes. The mixture of isomers consists primarily of three dimethylbenzene isomers (ortho-, meta-, and paraxylene) and ethylbenzene. The feedstocks used for the development of xylene give rise to a combination of the four isomers (Fabri, U. Graeser, T. Simo, 2002). Of the three isomers, para-xylene has the largest demand by far.

In fact, p-x is oxidized into terephthalic acid, which can be esterified into dimethyl terephthalate (a polyester precursor). O-x is oxidized into phthalic anhydride (plasticizer precursor) and m-x into isophthalic acid (polyester precursor). EB is dehydrogenated into styrene, converted to polystyrene and other polymers (J.J. Jeanneret, A.R. Meyers, 1997; Fabri, U. Graeser, T. Simo, 2002). These isomers boil together so carefully that it is not necessary to isolate them by traditional distillation (J.J. Jeanneret, A.R. Meyers, 1997). In particular, the high-purity separation

Three primary processes: crystallization, adsorption, and a hybrid crystallization / adsorption process (M. Minceva, A.E. Rodrigues, 2007) are industrially conducted by p-x from a blended xylene blend. Approximately 60% of the p-x generated worldwide, however, is through adsorption technology.

Simulated Moving Bed (SMB) technology is used to perform adsorption systems , providing constant isolation using zeolites shared with cations such as Na^+ , K^+ , Ba^{2+} (Fabri, U. Graeser, T. Simo, 2002; D.B. Broughton, C.G. Gerhold, 1961; D.M. Ruthven, M. Goddard, 1986). In order to provide tools for process understanding, operations and optimization, this process is being researched and simulated (M. Minceva, A.E. Rodrigues, 2007; P.S. Gomes, M. Minceva, A.E. Rodrigues, 2008). A Simulated Moving Bed Reactor (SMBR) implemented for p-xylene output, xylene isomerization integration and selective adsorption running in the liquid phase (M. Minceva, P.S. Gomes, V. Meshko, A.E. Rodrigues, 2008; G. Bergeot and al., 2010).

The ordered mesoporous silica substance, so called mobile composition of matter (MCM-41), with a 2D hexagonal $p6mm$ shape, has many advantages as an absorbent, including a wide surface area, uniform pore distribution (approximately 2.5 nm) and ordered mesoporous channel structure. Its mesoporous surface has quantities of

hydroxyl functional groups (Si-O-H) that can be modified by O-H grafting with various functional groups and greatly extends its use. For example, the recorded mesoporous silica-based materials modified with functional groups of amine and thiol have been shown to be especially effective in sequestering heavy metals from water (Mercier and Pinnavaia, 1997). Moreover, the strong performance of unmodified and modified mesoporous materials using alkyl groups on organic pollutant adsorption was achieved (Baccile and Babonneau, 2008; Wang and Tan, 2007).

As a matrix, the mesoporous MCM-41 can be used to build an implantable drug delivery device (Vallet-Regi et al. , 2001; Munoz et al., 2003). It has also been applied for catalytic cracking because of its ample acid sites and high cracking activity. The MCM-41 has so far been primarily used for the adsorptive removal of heavy metals and common organic contaminants, medical transmission and catalytic cracking (Walcarius and Mercier, 2010; Arica et al., 2017). (2010: Manzano and Vallet-Regi; 2017: Roika et al.). In the previous works they focused on the adsorption equilibria of xylene isomers and ethylbenzene in a microporous metal–organic framework, in the other side, this work aims to investigate the use of mesoporous silica material such as MCM-41 as an adsorbent due to their low cost and also for their big stability.

I.2 Objectives

In this work we are going to:

- To consists in the study of MCM-41 mesoporous adsorbent for separation of xylene isomers.
- Adsorption equilibrium isotherms will be collected by performing a set of single- and multicomponent (binary and quaternary) breakthrough experiments to measure adsorption equilibrium isotherms and selectivities.
- Modelling the adsorption data.

II. Adsorption

In the 18th century, the ability of porous solids to reversibly adsorb large volumes of steam was recognized and the first experiments were carried out by Scheele and Fontana (Mc Brain, 1932), but at the level of separation and purification, the functional use of this property for large-scale industrial projects is comparatively recent (Ruthven, 1984b). The first concrete steps were made in the 1950s with the use of adsorption as a way of splitting mixtures into two or three sources, each enriched with a value-added compound they would like to retrieve.

The first examples in this area were provided in that decade with the Arosorb method for the recovery of aromatic hydrocarbons (Davis et al., 1952) and with a variety of processes. At the beginning of the 1960s, adsorption was used to distinguish linear paraffins from branched and cyclic isomers. There was a substantial growth in the range and size of these processes in the 1970s. Figure 1 shows the pattern of the adsorption process.

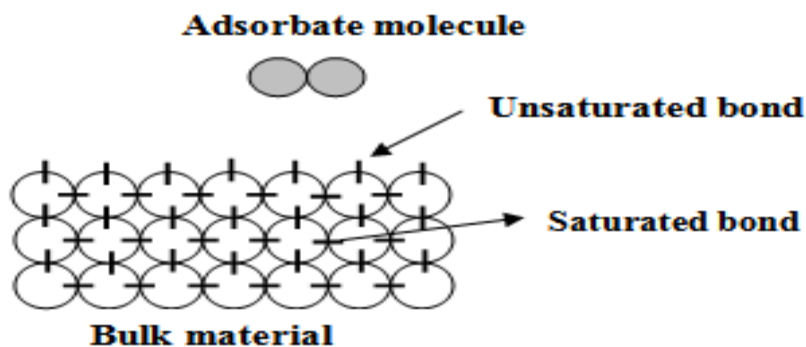


Figure 1: Schematic representation of the adsorption process (D.M. Ruthven, 1987)

II.1 Adsorption Balance of Pure Components

Adsorption balance information is the most relevant information for understanding the adsorptive mechanism. Irrespective of the number of components present in a given structure, the adsorption equilibrium of pure components is a crucial ingredient in the understanding of how these components work within a solid adsorber. This knowledge can be used in the kinetic analysis of pure component adsorption, in the adsorption balance of multicomponent systems, and later in the adsorption kinetics of multicomponent systems (Duong, 1998).

II.1.1 Langmuir Equation

Langmuir (1918) was the first person to suggest a coherent theory of flat surface adsorption based on a kinetic point of view, a continuous method of "bombing" molecules to the surface and subsequent evaporation (desorption) of the surface to sustain a rate of zero surface accumulation in the equilibrium.

The assumptions of Langmuir's theory are the following:

1. The surface is homogeneous, the energy being constant in all sites
2. The adsorption on the surface is located, the adsorbed atoms or molecules are adsorbed in localized and defined sites
3. Each site can only accommodate a single molecule or atom, which should not interfere with the neighboring molecules or atoms.
4. Langmuir's theory is based on a kinetic principle, i.e.

The rate of adsorption correlates to surface desorption values. Equation 1 is the famous Langmuir equation. The equation presented is written in terms of quantity adsorbed (C. Malara, G. Pierini, A. Viola, 1992).

$$q = q_s \frac{bP}{1+bP} \quad (1)$$

Where

$$b = b_0 \exp\left(\frac{\Delta H_0}{RT}\right) \quad (2)$$

The letter q symbolizes the quantity of adsorbed (g/100 g ads), q_s symbolizes the overall quantity of adsorbed corresponding to the monolayer saturation, b represents the constant affinity and is temperature-dependent and P represents the adsorbate partial strain.

Another way to present the Langmuir equation is in terms of the adsorbed fraction (θ).

$$\theta = \frac{bP}{1+bP} \quad (3)$$

Isothermal Langmuir is not always confirmed, mainly on the assumption that all active surface sites have the same adsorption heat. If the surface is saturated, adsorption heat typically decreases, meaning that the surface is not homogeneous and more assets are filled as a matter of priority by adsorption sites (Xomeritakis, G., Lai, Z., and Tsapatsis, M. 2001).

The parameters of the Langmuir equation can be obtained from equation 4

$$\frac{1}{q} = \frac{1}{q_s bP} + \frac{1}{q_s} \quad (4)$$

II.1.2 Dual-Site Langmuir (DSL)

The ideal Langmuir model returns an appropriate response to the actions of the low-pressure system in many systems, but fails in the saturation field where molecular interaction effects are pronounced. Due to either the heterogeneity of active sites or the interaction of adsorbed molecules, deviations may occur.

One of the variants due to energy heterogeneity is the Dual-Site Langmuir (DSL) model, equation 5, which identifies two types of active sites on the solid, with each active site adopting a "Langmuirian" action (Yan, Y., Davis, M., and Gavalas, G. 1995).

$$q = q_s^C \frac{b^C P}{1+b^C P} + q_s^J \frac{b^J P}{1+b^J P} \quad (5)$$

II.2 Isosteric Heat of Adsorption

The isosteric heat of adsorption, which is the ratio between the infinitesimal difference in the adsorbate enthalpy and the infinitesimal variation in the adsorbed number, is one of the basic quantities of adsorption studies. In clinical trials, knowledge of the heat produced is relevant because as heat is released into adsorption, the energy released is partially absorbed and partially dissipated into the environment by the adsorbent solid.

Due to this rise in temperature, the portion consumed by the solid raises the temperature of the particle and decreases adsorption kinetics as it is governed during adsorption by the rate of cooling of the particle. Therefore in the study of adsorption kinetics, knowledge of isosteric adsorption heat is significant (Yuan, W., Lin, Y., and

Yang, W. 2004). Isotheric heat may or may not differ with the amount of adsorption and is measured using the van't Hoff thermodynamics equation below:

$$\frac{\Delta H_{st}}{RT^2} = \frac{\partial \ln P}{\partial T} \quad (6)$$

II.3 Adsorption Balance Multicomponent

When two or more adsorptions arise in a device with the possibility of sharing the same adsorber surface, the adsorption is viewed as a multi-component, making the isotherms more complex. In this situation, interactions between different species of adsorbate are of critical importance. The needed information on multi-component equilibrium is most generally gathered from single-component isotherms because of the difficulty of obtaining experimental data, including for simpler multi-component structures. (Xomeritakis, G., Lai, Z., Tsapatsis, 2001).

II.3.1 Langmuir Multicomponent Equation

This presents the application of the Langmuir Equation to N-species systems. The principles of this expansion are the same as those of the monocomponent equation (C. Malara, G. Pierini, A. Viola, 1992).

Equation 7 is explicitly presented in order of the amount adsorbed.

$$q = q_s \frac{b_i P_i}{1 + \sum_{j=1}^N b_j P_j} \quad (7)$$

This equation is known in literature as the Langmuir extended equation and returns the quantity adsorbed by the I species in the multi-component scheme. The multi-component Langmuir equation is thermodynamically compatible only if the saturation potential is equivalent for all organisms.

II.3.2 DSL Multicomponent Equation

Like the Langmuir model, the Langmuir Dual-Site model can also be extended explicitly from the single component model (Yan, Y., Davis, M., and Gavalas, G. 1995).

$$q = q_{si}^C \frac{b_i^C P_i}{1 + \sum_{j=1}^N b_j^C P_j} + q_{si}^J \frac{b_i^J P_i}{1 + \sum_{j=1}^N b_j^J P_j} \quad (8)$$

This equation implies energy heterogeneity, distinguishing two categories of sites active on the solid, following each active site a "Langmuirian" behavior.

III. Xylene Isomers

Xylene isomers are aromatic compounds derived from petroleum oil. The molecular structure of these isomers consists of one benzene ring and two methyl groups bound to the ring in three distinct positions. The word xylene is widely used to designate the industrial combination of the three isomers, ortho-xylene, meta-xylene and para-xylene; or 1,2-dimethylbenzene, 1,3-dimethylbenzene and 1,4-dimethylbenzene, respectively (Health Canada, 1986). Because these compounds are isomers and have identical physicochemical properties, the process of producing pure isomers is complex. Its related industrial applications, especially in the plastics industry, have led to the development of a number of studies focusing on the use of new materials. These studies have the goal of refining current processes that aim to acquire pure isomers, with a focus on improving the separation performance of xylene isomers.

Xylene isomers are derived from the catalytic phase of naphtha reformation resulting from the main distillation of petroleum. In this process, isomers are isolated from other hydrocarbons by a catalytic wheel containing platinum halogen. The development of pure xylene by the petrochemical industry begins with the isolation of a fraction composed of eight carbon atom hydrocarbons, the C8 fraction that feeds the xylene column.

The effluent from this xylene column will then be fed to the PAREX unit to obtain p-xylene (extract). The refined oil is pumped into the ISOMAR unit, where the isomers are converted into p-xylene. After this point, the unused materials returned to the xylene column (Meyers, 2003).

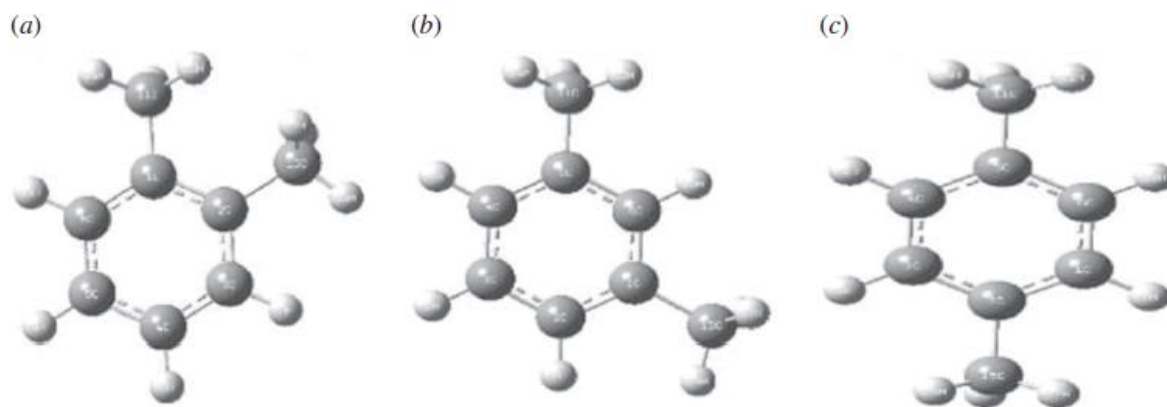


Figure 2: Molecular structures of (a) o-xylene, (b) m-xylene and (c) p-xylene
(Muhammad Farooq Saleem Khan and al., 2018).

III.1 the Importance of Separating Xylene and Ethylbenzene Isomers

The term xylene refers to the group of three benzene compounds, which comprises ortho-, meta- and para-xylene, both dimethylbenzene isomers. Xylenes are present in coke gases, in gasses formed by dry distillation of wood (hence the name: xylon means wood in Greek) and in oil. Xylenes Treatment is colorless, fragrant and friendly, but with poisonous properties, and can induce headache, decrease muscle strength, dizziness and changes in the sense of balance.

High levels may induce dermis inflammation, trouble breathing, lung, liver and kidney problems, and may contribute to elevated urine levels. In serious situations, the kidneys may also cause death. Xylene isomers are used on a wide scale as synthetic solvents or as intermediates for certain derivatives (Deckman et al., 2007).

III.2. the Para-, Meta- and Ortho-xylene

a. The Para-xylene

Para-xylene or more generally, p-xylene (pX) is an aromatic hydrocarbon based on a benzene ring containing two methyl replacements. "p" stands for and specifies the role of the methyl group which in the case of pX, is at positions 1 and 4 respectively. The IUPAC name is 1, 4-dimethylbenzene. Of the three isomers, pX has the highest market, largely due to the new polyester industry. PX is mostly used for the processing of distilled terephthalic acid (PTA) and terephthalate esters, such as dimethyl terephthalate (DMT), which is used in the construction of various polymers such as

Polyethylene terephthalate (PET), polypropylene terephthalate (PPT) or polybutylene terephthalate (PBT). Various grades of PET are used for a wide variety of common consumer products, such as film, synthetic fiber and plastic bottles for drinks. PPT and PBT can be used to render identical goods with different properties (Deckman et al., 2007).

The pX dime, di-p-xylene, when Polymerized forms Parylene, the trade name for poly para-xylene. In electronics, the low-pressure chemical vapor deposition of Parylene produces a thin film of adaptive insulation. Parylene coating has a high electrical resistance and is resistant to moisture infiltration. One of the most recent uses of parylene is in pharmaceutical applications to have an inert buffer against moisture, toxins, bio-fluids and biogas (Yuxi Yang et al., 2017).

It also has a high degree of bio-compatibility required for implants and other long-term applications. It is used as a dielectric in certain high-performance capacitors for precise calculation. It is also used for the storage of document records.

b. The Meta- and Ortho-xylene

M-xylene (mX) is an aromatic hydrocarbon based on a benzene ring comprising two methyl equivalents in positions 1 and 3 of the aromatic ring. The IUPAC name is 1,3-dimethylbenzene. Economic interest in this isomer is due to its use in the manufacture of isophthalic acid or benzene-1, 3-dicarboxylic acid, an aromatic dicarboxylic acid with the chemical formula $C_6H_4(COOH)_2$. It is an isomer of phthalic acid and terephthalic acid and can be obtained by oxidation of mX with chromium. Isophthalic acid is used as a copolymer to change the properties of polyethylene terephthalate (PET) and to make PET more suitable for the manufacturing of soft drink bottles (Deckman et al. 2007)

The distinction with the other isomer, o-xylene (OX), is that the two methyl replacements are in the 1 and 2 aromatic rings. Its IUPAC designation is 1,2-dimethylbenzene. OX is commonly used in the manufacture of phthalic acid, which can be produced by catalytic oxidation of OX with oxygen. O Phthalic acid in its anhydrous nature is commonly used in the agricultural processing of dyes, insecticides, plasticizers and pharmaceuticals, often used in analytical chemistry.

III.3 Processes for the Separation of Xylene Isomers

The isolation of xylene isomers is a classic issue in the petrochemical industry since its boiling points are very close. The first separation methods were focused on the isolation and crystallization of solvents (Minceva and Rodrigues, 2003).

The raw materials used in the manufacture of xylene (catalytic reformed, gasoline pyrolysis, toluene dismutation) include a combination of xylene and ethylbenzene (EB) isomers. The standard balance compositions of these compounds in the separator power supply are seen in Table 1.1 (Minceva and Rodrigues, 2005b).

Fractional distillation is a common process used in many industrial plants to isolate chemical compounds using the physical properties of the boiling point. Can be used for the separation of oX and probably EB, but not for the separation of pX. However it is also difficult to use this technology as traditional fractional distillation to isolate EB and the different xylene isomers effectively and economically. This is because the boiling points of the four aromatics are within a very small range of $8 \pm ^\circ\text{C}$, from $136 \pm ^\circ\text{C}$ to $144 \pm ^\circ\text{C}$ (see Table 1).

Tableau 1. Balancing compositions and physical properties of xylene isomers and ethylbenzene (Krishna, R. 2015). 241614

compounds C8	mass composition %	boiling point ($\pm^\circ\text{C}$)	melting point ($\pm^\circ\text{C}$)
Ethylbenzene	14.0	136	-95
Meta-xylene	49.7	139	-48
Ortho-xylene	12.7	144	-25
Para-xylene	23.6	138	13

The pX and mX boiling points are only $1 \pm ^\circ\text{C}$ apart. As a result, it would be necessary to large equipment, significant energy consumption and/or substantial recycling in order to obtain separations of effective and satisfactory xylenes. Nevertheless, several methods and processes, other than the simple fractional distillation have been developed and tested to separate these aromatic compounds C8 and some are successfully practiced on an industrial scale. Examples include fractional

crystallization, adsorption and combinations of these. Fractional crystallization in a crystallizer takes advantage of the differences significant between the melting points and solubilities of C8 aromatic compounds.

Tableau 2. Physical Properties of C8 Aromatics (Yuxi Yang and al., 2017):

	PX	MX	OX	EB
kinetic diameter (Å)	6.7	7.1	7.4	6.7
boiling point (K)	411.5	412.3	417.6	409.3
freezing point (K)	286.4	222.5	248.0	178.2
dipole moment (D)	0	0.36 (liquid)	0.62 (gas)	0.59
polarizability (cm³)	13.7	14.2	14.9	14.2
density at 298 K (g cm⁻³)	0.858	0.861	0.876	0.867

IV. MCM-41

The MCM is a suitable device for the study of confined fluids and is also commonly used for fundamental studies (Kresge, Leonowicz et al. 1992; Lin and Mou 1996). One of the most researched members of the series is the MCM-41.

The huge interest in the MCM-41 is focused on its simple, regular and modular construction. This silicate has a hexagonal, unidirectional arrangement of cylindrical pores. The diameter of the cylindrical pores can be adjusted between 2 and 10 nm. In fact, this mesoporous content is obtained by condensation of amorphous silica (SiO₂) in water helped by the self-assembly of surfactant mice. The porosity geometry obtained is then determined by the imprinting of the hexagonal crystal-liquid process of the surfactant, which plays the role of the structuring agent. (2010, Adjdir).

The MCM-41, which has a typical hexagonal pore network with a well-defined pore size and a very high specific surface area often reaching 1000 m²/g and a high chemical and thermal stability, has been the most studied and used.

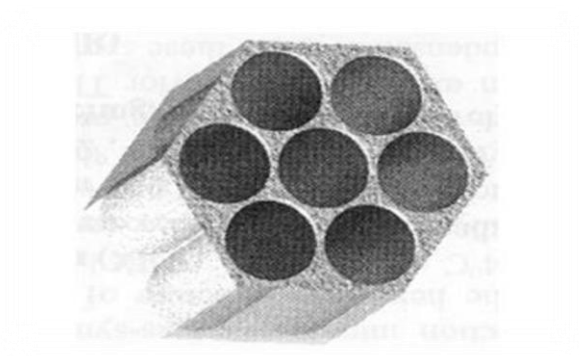


Figure 3 : Schematic representation of MCM-41 (Adjdir, 2010).

IV.1 the different methods of MCM-41 synthesis

Since the discovery of the M41S family of materials, a great deal of research has been dedicated to understanding the mechanism of their formation. The production of these materials is described by a number of conventional methods (based on the use of chemicals in the MCM41 synthesis) and by an unconventional method based on the use of natural sources such as clay, waste etc in the synthesis of our materials. (The Vincent, 1971).

IV.1.1 Conventional synthesis

In 1971 (Vincent 1971) the synthesis of low-density silica by hydrolysis and condensation of tetraethylorthosilicate (TEOS) in the presence of a cationic surfactant (Di Renzo, Cambon et al. 1997) was described in a patent and it was established in 1997 that this work was the first synthesis of a mesoporous silicic material.

Mesoporous silica of type MCM-41 is very well structured with a hexagonal mesoporous network and has a large pore volume. However it is not easy to control grain size and polydispersity at the nanometer scale. It was not until the first work (Sadasivan, Fowler et al. 2002) that monodisperse mesoporous silica nanoparticles (MCM-41) were obtained. These nanoparticles were prepared by rapid ground neutralization of TEOS hydrolysis-polycondensation carried out in the base NaOH medium in the presence of the surfactant CTAB. In the synthesis of MCM-41 there are four necessary elements that are used :(Kresge, Leonowicz and al. 1992):

1. An anionic, cationic, nonionic or neutral surface-active molecule (structuring agent) to direct the final structure of the material (hexagonal, cubic, lamellar).
2. A source of silica (fumed silica, sodium silicate, TEOS, TMOS....).
3. A solvent (water, ethanol....).
4. An acid according to the desired synthesis.

IV.1.2 Unconventional synthesis

Silica is a naturally occurring material in minerals such as quartz and silica sedimentary rock, in plants such as bamboo, rice and barley. However the majority of the silica used in chemical applications is of synthetic origin. Silica is used as a material in many applications due to its wide range of structures and physico-chemical properties, which are highly dependent on synthetic processes. Irina P. Beletskayab,2005).

Silica (silicon dioxide) is the name given to the group of minerals made up of silicon and oxygen, the two most abundant elements in the earth's crust; in fact, silica accounts for more than 60% of the earth's crust. (The Miguel Yusa,2005).

It occurs naturally in a variety of forms: sedimentary rocks, metamorphic rocks and magmatic rocks. Silica occupies an exceptional place among oxides due to its crystal-chemical characteristics, its genesis method and its petrographic importance. (Francisco Alonso,2005)

It is commonly considered in a crystalline form, but can also be found in an amorphous (non-crystal) state. Crystalline silica is hard and chemically inert and has a high melting point. These attributes are sought after for a variety of industrial applications. There are two sources of silica:

a) Natural source

Silica occurs in the Free State in a crystalline or amorphous form and in a mixed state as silicate. In nearly all its forms, it exists as the simplest model of tectosilicates: a three-dimensional structure consisting of SiO_4 tetrahedral connected to each other by its vertex, with each oxygen atom being common to two tetrahedrals, thus the overall SiO_2 formula. (Chauvel and Monnier in 1967)

Natural silica can be derived from many natural products, such as clay, which is a decomposition product of silica rocks and includes phyllosilicates (sheet silicates).

Clay is often born from the weathering of minerals, and then undergoes a perpetual evolution over time on a geological basis, moving from one clay mineral to another and modifying its original environmental properties. Clay particles are usually the result of physical or mechanical disintegration of minerals, accompanied by chemical transformation.

Raw clay contains very small elementary particles that reflect crystalline individuals (pure mineral phase), called clay minerals liable for their properties known as swelling and absorption properties (Chauvel and Monnier 1967). When clay is in contact with water, it becomes sticky and plastic (malleable).

b) Synthetic source

Amorphous silica is typically of industrial origin, with the exception of diatomaceous soils. This form of silica is the most impaired and therefore the most reactive. The most popular model to explain amorphous silica is that it consists of rings of silicone atoms bound to each other by bridging oxygen atoms. Despite the non-periodicity of its lattice, amorphous silica maintains the tetrahedral environment of silicon atoms and can be found as a structural medium to enhance mechanical properties, as a catalyst help (Johnson and Stein 2001), as a separating agent in chromatography, or as a functionalized material when surface silanols react with a given molecule, in particular for biological use.

IV.2 Deformation mechanism

The great resemblance of the final structures to the observed crystalline phases... in pure surfactant solutions gives the mechanism formulation (LCT) where the polymerized silica on the surface of the liquid crystal phases formed by the aggregation of the surfactant (Zhang, W., T. R. Pauly, and al. 1997).

However, the researchers have still not been able to explain the fact that the synthesis of the mesoporous materials is carried out with low concentrations for the formation of the liquid crystals (Auvray, X., C. Petipas, and al. 1989).

However, an alternative mechanism has been proposed under different models, it suggests that the interaction between silicates and surfactants acts as a force that leads to the formation of structures that determine the final nature of mesoporous materials. (Luechinger, M., L. Frunz, and al. (2003).

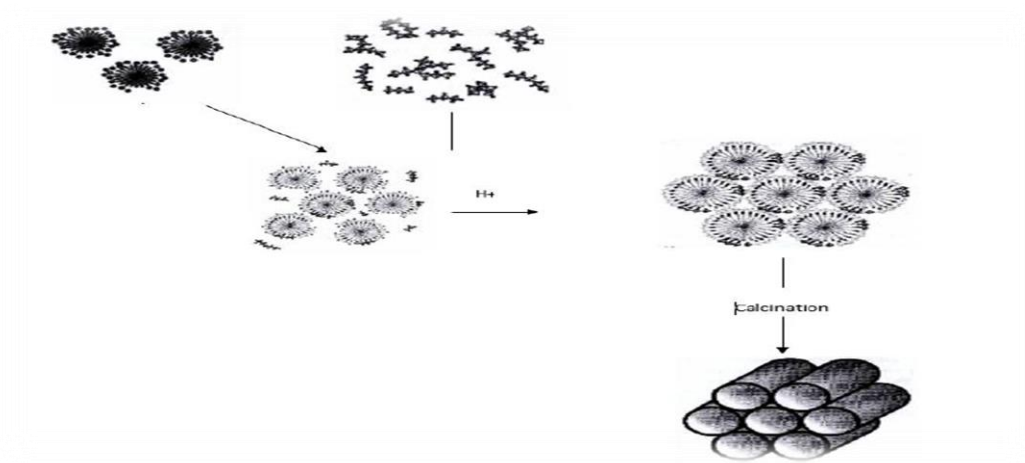


Figure 4 :Diagram of the forming mechanism according to Luechinger, M., L. Frunz, and al. (2003).

IV.3 Properties of MCM-41

IV.3 .1 Surface properties of silica

The reactivity of silicate materials is mainly due to their surface properties. The knowledge of these properties is essential to understand and control the reactions occurring in contact with these materials. There are two main families of functional groups on the surface of silica:

- a. Siloxane groups.
- b. Silanol groups.

A detailed description of these groups and their properties was carried out in the thesis of (Despas 1998).

a) Siloxane group

The siloxane groups are bridges (Si-O-Si) resulting from the condensation of two neighbouring silanols. They are hydrophobic and not very reactive. They are hydrophobic and not very reactive. Their formation is favored at high temperature during silica dehydration. **(Figure 5).**

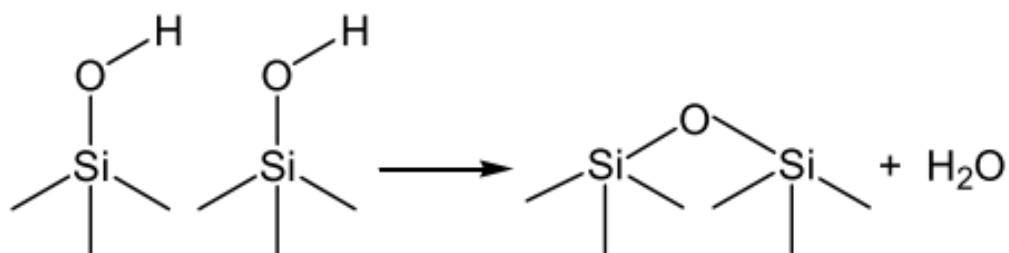


Figure 5: Formation of a Siloxane bridge by condensation of two Silanol groups (Despas 1998).

These groups can be used for the retention of non-polar molecules, but the proportions thus retained are too small to be used as a stationary phase in chromatography, for example.

b) Silanol groups

Silanol groups condition the reactivity of silica. Indeed, they prove to be acid-base and adsorption sites, but they are also involved in silica functionalization processes.

There are several types of Silanol groups among which free silanols are considered the most reactive.

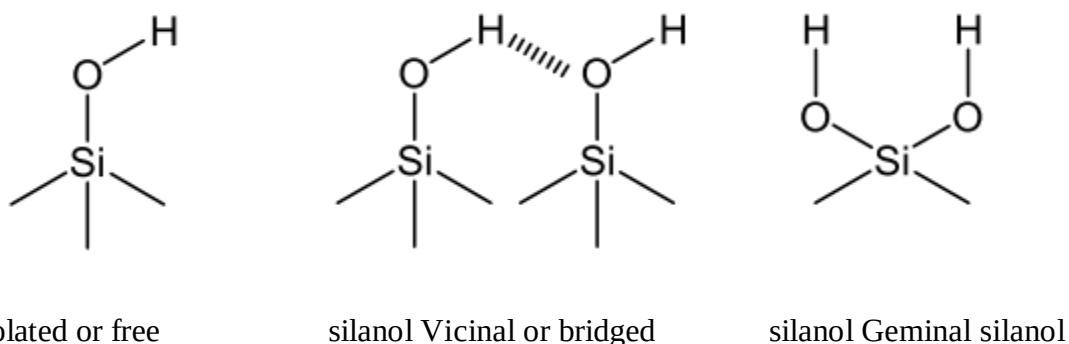


Figure 6 : Schematic diagram of the main types of Silanol groups (Kondo, Igarashi and al. 1992)

The number and the nature of the groups condition the reactivity of silicas. It is established that isolated groups are by far the most reactive (Kondo, Igarashi and al. 1992); Titova and Kosheleva 1992). The free silanol groups are thus able to intervene in the adsorption of amino molecules (Titova and Kosheleva 1992; Van Cauwelaert, Vermoortele et al. 1971) but also of metallic species like Hg^{II} (Tiffreau, Lützenkirchen and al. 1995; Walcarius, Devoy and al. 1999).

IV.3 .2 Hydrophobia/ surface hydrophilicity

The surface of the MCM-41 is very different from the surface of microporous zeolites. In the case of MCM-41, the inner surface of the pores corresponds to the cross section of an amorphous silica network, and is as rich in Silanol as the surface of a normal silica gel. IR spectroscopy shows that separate areas of the isolating (hydrophobic) Silanol groups at 3745 cm^{-1} and adjacent (hydrophilic) Silanol groups 3500 to 3750 cm^{-1} are present on the surface and that hydrolysis of the Siloxane bridges by adsorbed water increased the concentration of Silanol groups and hydrophilicity (Tiffreau, Lützenkirchen and al. 1995).

IV.3 .3 Pore size

Mesoporous materials are characterized by a regular distribution of their pores. The final size of these pores is directly related to the length of the alkyl chain of the structuring agent since the first communications on the MCM-41, the greatest pores can be formed when auxiliary organic products are added to the preparation. In practice, the addition of oil allows the formation of swollen micelles that participate in the formation of mesophases with a larger unit cell. Nature of oil affects the efficiency of micelle swelling. The largest pores are obtained when organic 1, 3, 5-trimethylbenzene (TMB) products are added to the preparation as follows swelling agent (Sayari, A. and Y. Yang 2000) have reported that swelling can be achieved by fatty amines. (Blin and al. 2000) achieved a remarkable expansion of MCM-41 with decane by adding PEO-PPO-PEO triblock copolymers leave the oil in the surfactant solution. Form mesoporous materials with pores larger than those formed by surfactants (Zhao, D., Q. Huo, et al. 1998).

Syntheses of Si-MCM41 and Al-MCM41 by using the new co-structuring agents such as methylamine, dimethylamine, ethylamine and diethylamine instead of NaOH and TMAOH have succeeded in demonstrating that:

- To synthesize good quality materials using weak bases (amines).

- To facilitate the incorporation of Aluminum in the absence of alkali cations.

IV.3 .4 Wall Thickness

Mesoporous materials of the MCM-41 type have an amorphous silica wall called thickness, resulting from polymerization and polycondensation of silicate species in solution. This thickness, which determines the thermal stability of mesoporous materials, can vary between 5 Å and 20 Å. And the thickness of this wall has a direct influence on the hydrothermal stability of our material (Tang, F., L. Li, and al. 2012).

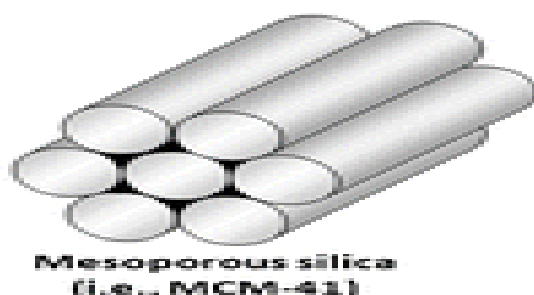


Figure 7: Wall thickness of the MCM-41 (Tang, F., L. Li, and al. 2012).

IV.3.5 Hydrothermal stability

Mesoporous materials such as MCM-48 and MCM-41 have poor hydrothermal stability in aqueous solutions or water at elevated temperatures. (Chen, Li and al. 1993)

(Kim and Inui 1996) studying the X-ray diffraction pattern of calcined MCM-41 and MCM-48 heated to 343 and 373 K in water, noted that all samples lost a large part of the order at long distance and the mesh unit decreases when heated in water at 343 K for 12 hours.

The decrease in material mesh parameter (Lewandowska, Monteverdi and al. 2002) and the increase in surface hydrophobicity both caused by condensation of silanol groups are two consequences of high-temperature calcination. (Van Der Voort, Ravikovitch and al. 2002).

IV.3 .6 Insertions of heteroatoms

The discovery of mesoporous materials of the M41S family in 1992 opened up the field for the use of these materials as carriers for various metals and other catalytically active species (Beck, Vartuli and al. 1992).

After their first synthesis, many laboratories incorporated various elements other than silicon into the framework of MCM-41: aluminium, vanadium, niobium, etc., thus changing the physico-chemical properties of the material (Lewandowska, Monteverdi and al. 2002). With the incorporation of various metals (Ni, Al, Co, Mg, Fe, Cu), it was found that the catalytic properties of these materials could be improved (Occelli, Biz and al. 1999; Corma 1997).

Many researchers have successfully incorporated metals into MCM-41, Iron(Tuel 1999), Titanium (Corma, Navarro and al. 1994), Vanadium(Corma 1997), Chromium, Copper, Zinc(Wu, Hu and al. 2001). The stability of the products on calcination depends not only on the nature of the incorporated element, but also on the conditions of synthesis(Tuel 1999). The presence of a metal in the walls of mesoporous materials has made it possible to carry out studies on specific reactions, such as hydroxylation and alkylation of phenol (Savidha, Pandurangan and al. 2004), oxidation and isomerization of hexane(Carvalho, Wallau and al. 1999).

IV.3 .7 Copper insertions

Several works on mesoporous materials have concerned the incorporation of copper (Wu, Hu and al. 2001) have studied the effect of copper content on the catalyst, the effect of UV photons, and the mass of the catalyst in photo-oxidation reactions.

(Hadjiivanov, Tsoncheva and al. 2003) prepared Cu-MCM-41 and Cu-MCM-48 by two methods:

- By impregnation in a solution of Cu (II) acetyl acetate in the presence of chloroform.
- By impregnation in an aqueous solution of copper nitrate.

The two materials are characterized by different analytical techniques. It has been found that the amount of Cu⁺ in Cu-MCM-41 is higher than in Cu-MCM-48 which explains the difference in activity in the methanol decomposition reaction (Hadjiivanov, Tsoncheva and al. 2003).

(Chengli Huo, Jing Ouyang, and al.2014) prepared CuO-MCM-41 by the direct method (insertion of copper during synthesis) and comparing it with Si-MCM-41, noted that it is less ordered and that copper oxide is only found in the outer surface of the materials as no copper is detected in the mesopores.

The authors explain this by the pH of the basic solution which causes the precipitation of $\text{Cu}(\text{OH})_2$. This precipitation will prevent the encapsulation of copper in the amorphous walls of MCM-41. In addition, the pores of MCM-41 are occupied by surfactant micelles that can also prevent the introduction of copper into the pores. Copper oxide is formed during calcinations of the synthesized materials and is localized on the outer surface of MCM-41 (Chengli Huo, Jing Ouyang, and al.2014).

IV.4 Applications

Mesoporous materials are nowadays obtained in various forms: first synthesized in powder form, they are now found in the form of solid materials (Kisler, Gee and al. 2003), fibres (Namba, Mochizuki and al. 1998), thin films or aerosols (Kang and Rhee 2005). These various forms and constituents naturally allow a very large number of applications for these materials, which is further increased by the possible functionalization of pores or walls. The most cited applications are those exploiting the enormous specific surface area offered, or the controlled nanometric size of the pores, in fields such as catalysis, filtration, depollution or sensors (Sayari and Yang 2000). Organized mesopores can also be used for the growth of nanoparticles of controlled size (Beck 1991).

a. Adsorption and separation

The MCM-41 is one of the mesoporous materials that occupy a unique position as a reference for the study of adsorption in mesopores. The homogeneous distribution of the pore size allows more precise studies of the physics of adsorbed phases (Ravikovitch, P., S. Ó. Domhnaill, and al. 1995). Adsorption properties are critical for applications in separation. The control properties of the fluid in the ordered channel can develop new applications.

Indeed, uniform pore size is an important factor in several chromatography and separation methods. For example, the use of mesoporous materials structured with column surfactants in: the exclusion chromatography, normal phase HPLC (Grün, M., A. Kurganov, and al. 1996) phase chromatography and enantioselective HPLC (Thoelen, C., J. Paul, and al. 2000). The control of the structure of materials and in of its spherical morphology are determining parameters for the successful applications in chromatography (Grün, M., I. Lauer, and al. 1997). The selectivity of the nanometre has been able to open up new applications in the separation of molecules biological.

In the field of porous materials, the MTS (Micelle-TemplatedSilica) should compete with well-established materials such as zeolites and silica gels. Their special properties can open up new fields of application, but the question is whether the improvement of methods by porosity control justifies the choice of new equipment instead of conventional. In the field of storage of hydrogen, several works have been carried out in this field change the metals of transitions incorporated for the best adsorption rate (Wu, C., Q. Gao, and al. 2009).

b. Acid catalyst

The use of mesoporous solids as a catalyst for acid-base reactions requires the insertion of aluminum into the structure of the MCM-41. It has been shown that the tetrahedral aluminium which is responsible for the catalytic activity, the rest of the structure allowing an efficient circulation of the transformed chemical species and a surface of significant exchange. Within this framework, all efforts have been directed towards increasing the ratio between the number of silicon atoms and the number of aluminium atoms in the MCM. The researchers arrived at a report of 2. The problem of modifying the structure during calcination was then discussed; the number of tetra coordinates decreasing after calcinations. (Auroux, A. 2002)

Mesoporous materials have been extensively studied with respect to their use in cracking and hydrocracking reactions. Unfortunately disadvantages of low acidity and low hydrothermal stability of catalysts MCM-41 reduce the benefits of pore accessibility even for large pores molecules. Nevertheless, MCM-41 catalysts show substantial activity for bulky substances such as palm oil and asphaltene (Byambajav, E. and Y. Ohtsuka, 2003). FSM silicas- 16 (FoldedSheets Mesoporous) are active in the thermal degradation of polyethylene in fuel oil (Uddin, M. A., Y. Sakata, and al. 1998).

For small molecules, such as 1-butene, n-hexane, n-heptane or cyclic hydrocarbons such as tetralin and decalin, the activity of MCM-41 is very high. Lower than zeolite beta, and comparable to that of amorphous aluminosilicates (Auroux, A. 2002).

Al-MCM-41 exhibits better activity in the Diels-Alder reactions for the large organic molecules compared to ZSM-5 and HY zeolites (Onaka, M., N. Hashimoto, and al. 2003). In the reaction cyclopentadiene with crotonaldehyde, MCM-41 grafted with

aluminum isopropoxide shows the highest activity compared to Al-MCM-41 prepared by the direct method.

c. Basic catalyst

Knoevenagel condensation can be done by using MCM-41 not calcined (Martins, L. and D. Cardoso 2007). The reaction of Michael (Aguado, J., D. Serrano, and al. 2000) and Claisen-Schmidt (Weckhuysen, B. M., R. Ramachandra Rao, and al. 2000) are catalyzed either by amines or by solids such as (HDTMA⁺), Si-MCM41 and Al-MCM41 after neutralization of the negative charge by Na⁺, Cs⁺.

d. Redox catalyst

There are numerous reports in the literature about redox reactions on modified mesoporous materials. In many cases, it is very difficult to evaluate the performance of such materials, because the reaction conditions are often not comparable. Ti-zeolites, such as TS-1, TS-2 and Ti-β, are effective catalysts in oxidation of a variety of organic compounds (Huybrechts, D., L. De Bruycker, and al. 1990), such materials have been known since the early '80s. Mesoporous titanium-containing materials as well as those containing modified with transition metals such as Zr, V, Cr, Mg, Fe and Cu are catalysts promising oxidation processes. Ti-MCM-41 was early studied as a catalyst of selective oxidation; such mesoporous materials have the clear advantage of a high pore system allowing the oxidation of a larger number of hydrocarbons.

Calcined Fe/SBA-15 catalysts in which only a small amount of Octahedral Fe³⁺ is detected show good selectivity in oxidation reactions alkanes, alkenes and arenas with H₂O₂ as an oxidant (Nozaki, C., C. G. Lugmair, and al. 2002). Mn-MCM- 41, prepared by the surfactant ion exchange method, show high activity for the epoxidation of stilbene (Yonemitsu, M., Y. Tanaka, and al. 1998). Co-MCM-41 and Ni-MCM-41 are active in the oxidation of benzene or the oxidation of styrene in the liquid phase to give phenol or benzoic aldehyde respectively with H₂O₂ as an oxidant (Parvulescu, V. and B.-L. Su 2001). Oxidative dehydrogenation (ODH) of alkanes to obtain alkenes by V-MCM-41 has also been reported (Junges, U., W. Jacobs, et al. 1995).

e. Catalytic support

The idea here is to functionalize MCM-41 with a catalyst; thus, the circulation of chemical species is greatly facilitated, and the reaction surface becomes much larger. For example, heteropolyacids such as H₃PW₁₂O₄₀ which have very acidic sites but a low

internal surface area, can be inserted into MCM-41, they then disperse in the entire material and this results in a very high reactivity. For example, the alkylation reactions of phenol groups with olefins are much faster with such a material than with pure HPA, and even faster than with H₂SO₄. Such a process also increases the selectivity of the reactions catalyzed in this way (Junges, U., W. Jacobs, and al. 1995).

f. Active principle

The MCM-41 are currently the object of remarkable interest for many uses in biology thanks to their important characteristics such as their unconnected cylindrical pores which can be used as reservoirs for active principles, the possibility of modifying their surface with numerous functional groups. (Nozaki, C., C. G. Lugmair, and al. 2002)

The addressing (or specific delivery) of therapeutic molecules to a diseased organ, tissue or cell is today a major challenge for the treatment of diseases, particularly infectious, cancerous or of genetic origin. Indeed, many active ingredients have physicochemical characteristics that are unfavorable to the passage of the biological barriers that separate the site of administration of the drug from its site of action. Other active molecules encounter enzymatic barriers leading to their degradation and rapid metabolism. Achieving therapeutically effective concentrations at the site of action can therefore only be achieved at the expense of significant loss of drug to other tissues or cells, resulting in significant toxic effects. For all these reasons, the development of drug delivery systems has gained considerable momentum in recent years. Among the vectors studied. Liposomes, nanospheres and nanocapsules are the most widely used. (Nozaki, C., C. G. Lugmair, and al. 2002).

CONCLUSION

Xylene isomers are important industrial raw materials, which usually come from naphtha crackers and reformers as a mixture. The xylene isomers mixture contains meta-xylene (m-xylene, MX), ortho-xylene (o-xylene, OX), para-xylene (p-xylene, PX) and ethylbenzene (EB), wherein o-xylene can be used for synthesizing phthalic acid, m-xylene can be used for synthesizing isophthalic acid or can be converted to p-xylene which is an important raw material for manufacturing polyester fibers, and ethylbenzene can be used for producing styrene monomer.

Because the xylene isomers have close boiling points, it is difficult to separate them by distillation. Actually, the separation of high-purity p-x from a mixture of mixed xylenes is industrially by three main processes: crystallization, adsorption, and a hybrid crystallization/adsorption process. In our case we choose to use adsorption as a method of separation between the xylene isomers and ethylbenzene. In this work I am going to use a mesoporous silica material MCM-41 as an adsorbent due to their low and economic cost and also for their big stability.

So in the laboratory i will study the adsorption equilibria of the mixture, also I am going to See the influence of the tow parameters Temperature and Pressure on this adsorption and the efficacy of the MCM-41 as an adsorbent in a different concentrations. the experimental data will be treated by the Dual-Site Langmuir model (DSL) and compare the results with the previous work's results which they obtained from the using of a different adsorbent (metal organic framework MOF) .

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