CATALYTIC PREPARATION, CHARACTERIZATION AND PERFORMANCE ISOMERIZATION OF *M*-XYLENE BY MODIFIED MONTMORILLONITE PREPARED BY MICROWAVE

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Abstract:

The preparation and the structural characterization of aluminium inter-foliated montmorillonite (Algerien clay) has revealed that calcination by microwave finish in 10 minutes, present results showed a similar characterisation of height performance as well as of classic calcinations (5 hours). The textural measurement of this four matrix shows that the decking of montmorillonite by the metallic polycations create an important micro porous system. The catalytic properties of this new solid micro porous using a transformation of the m-xylene as a test reaction, show a great selectivity of isomerisation by dismutation reaction to o- and p-xylene.

Key word: modified montmorillonite clay - xylene - isomerisation - microwave

1. Introduction:

The interest for Isomerisation of xylene, precisely m – xylene, in the last two decades was increased for two reasons, firstly due to the annual growth production of 6% to 8% of p- xylene (18 M tones per year) (Graph, 2003), a potential market for petrochemical industry (Tsapatsis, *et.al.*, 1999; Kapteijn, *et.al.*, 1997) secondly, the isomerisation reaction of xylene became a reference model for the characterisation of certain catalyst in order to verify their activities, stabilities and selectivities (Martens, *et.al.*, 1988; Morin, *et.al.*, 1996). These properties induced searchers to test a large number of zeolites with acid characters on the xylene transformation reaction.

A new family of solid micro porous to control porosity similar to zeolites called "pillared clay" had been developed and studied during the last 30 years (Vaughn, *et.al.*, 1979; Gil, *et.al.*, 2000). The rise of petrol price in 1973 stimulates researchers to synthesize new catalysts that are able to increase the crude fraction.

The inserted clays are obtained from montmorillonite by insertion of metallic polycations in the interlayer area (Figueras, 1988). After calcination at 773 K, the polycation inserted, is transformed in to pillar in the form of solid metal oxides cluster and developed to a great acidity (Schoonheydt, *et.al.*, 1999). The inserted clays by the hydroxy-aluminium polycations of the structure $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ containing Al_{13} are

interesting experimental model to test in the *m*-xylene isomerisation reaction model.

Aluminium clays are used in a lot of catalysis works, particularly in alkylation of benzene and toluene with methanol (Miller, *et.al.*, 1984), the dehydration of 2-propanol (Urab, *et.al.*, 1991) the hydro treatment of n-decane (Schutz, *et. al.*, 1985), dealkylation of cumene (Bradley, *et.al.*, 1993). It is known that the conversion depends directly on concentration of calcinations temperature of the catalyst. Acidity of the deck load to Al_{13} , is mainly connected to pillar and not to the kind of the clay (Figueras, 1988; Storaro, *et.al.*, 1996). This technique, allow the study of an area surface because it allow to distinguish acids areas of Lewis from Brönsted.

2. Raw materials and experimental technique

2.1. Preparation of based catalytic clay:

The source of material is the natural clay of Maghnia (Western of Algeria) consists of about 80% of montmorillonite, it was returned homoionic by the exchange of Na⁺ cation, named MMT-Na with cationic exchange capacity of 0.96 meq.g^{-1} .

The sodium montmorillonite was treated with (2 M) HCl solution with a weight ratio of 0.3, named MMT-H.

The synthesis of hydroxy- aluminium Al_{13} polymer was proceeded by adding drop by drop (1.5 ml/min) aluminium solution (AlCl₁₃.6H₂O) with definite concentration of (0.5M) NaOH solution with resulting concentration of (0.22 M) with ratio of OH/Al = 2, under continuous stirring for 3 hours then left 48 hours for ageing

of polymer. The Interfoliated solution is followed by adding drop by drop (2.4ml/min) to a suspension of montmorillonite MMT-Na or MMT-H of 1% with a ratio of Al/clay = 5mmole/g with a pH = 4.2. The argillaceous suspension obtained was filtered under vacuum, washed several times with distilled water, named MMT-Al and MMT-H-Al. These products were calculated by two processes, conventional and microwave. The conventional calcination occurs in a muffle furnace to programming of temperature 773 K during 5 hours bv temperature increasing of 2 °C/min, and the calcinations microwave method is achieved in a microwave furnace by temperature programming with a total power of 300 W during 10 min (De Andres, et.al., 1999).

2.2. Characterization of interfoliated clay.

The elementary chemical composition of sodium interfoliated clay was estimated by using fluorescence spectrophotometer type X 3400 Brucker-AXS. The specific surfaces of pillared clay were identified from isotherms of adsorption-desorption of N₂ at 77K by using micrometric device ASAP 2000. Products are previously vacuum gas free to 523K during 5 hours. The structure of clay interfoliated has been studied by XRD diffractometer PW 1800 PHILIPS endowed of a cathode of copper and a filter made of nickel using a stripe of copper ($\Box = 1.5418$ Å). The technique of sample preparation and the method of aggregates could

be summarized by putting some drops of the argillaceous suspension on a glass slide.

We let this solution to evaporate during 24 hours at room temperature. Thus, leaflets of the montmorillonite (sodium or in deck load) sediment preferentially following their faces. We obtain thin uniform thickness clay film glued to the partition of the glass. The acid properties of clays interfoliated to the aluminium were widely studied by the literature (Issaadi, *et.al.*, 2001; Belkhadem, *et.al.*, 2006).

To have an idea about the morphology of structure in leaflets of these clays interfoliated we took photos with an Electronic Sweep Microscope type (E.S.S.M) PHILIPS XL 30.

2.3. Catalytic test

The isomerisation reaction of the m-xylene is achieved in a reactor with bed stationary tubular Figure (1) under isotherm and isobar conditions containing 500 mg of catalyst. The reaction is studied in the cool catalyst conditions in the interval of temperature 473-673 K under atmospheric pressure in a current of nitrogen with a VVH of 2 h⁻¹. Products of the reaction are analysed by chromatography in sparkling phase using SHIMADZU type GC 17, provided with a detector of ionisation flame and a capillary column SE 30 of 25 m length and 0.25 mm internal diameter. Concerning the catalytic test by microwave, we used the same installation by substituting the classical oven by microwave ove

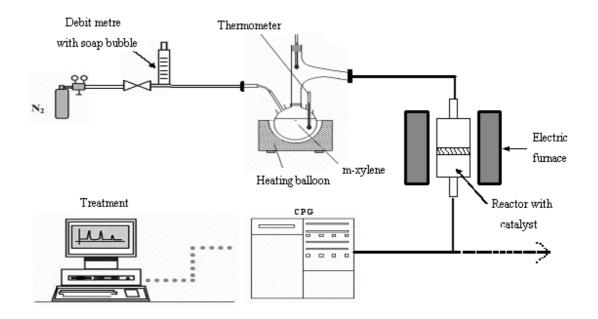


Figure (1): Diagram of the installation of the catalytic test in a classic oven

3. Results and discussions

3.1. Characterization

The compositions of samples are reported in Table (1), results of XRD and the textual measurements by the BET method are reported in Table (2).

Table (1): Chemical co	mposition of the sodium	montmorillonite MMT a	and the catalysts MMT-I	I-Al and MMT-Al

Composition (%yield)	MMT-Na	MMT-H-AI	MMT-AI
SiO ₂	62.5	64.56	59.89
Al ₂ O ₃	20.12	18.44	24.6
MgO	1.69	1.19	1.45
Fe ₂ O ₃	2.99	2.22	2.34
CaO	0.1	0.069	0.08
MnO	0.024	0.018	0.011
Na₂O	4.04	0.56	0.85
K₂O	0.98	0.69	0.85
TiO ₂	0.232	0.22	0.214
P ₂ O ₅	0.026	0.017	0.025
Cr ₂ O ₃	0.029	0.024	0.028
SO₃	0.03	0.02	0.03
ZrO ₂	0.025	0.019	0.022
SrO	0.0066	0.0038	0.0062
Rb ₂ O	0.091	0.0383	0.0402
PbO	0.004	0.0033	0.0036
ZnO	0.0162	0.0146	0.0155
CuO	0.0116	0.0096	0.0102
NiO	0.0339	0.0305	0.0319
BaO	0.0674	0.0657	0.0661
PAF	7.5	12.3	9.5
SiO ₂ /Al ₂ O ₄	3.1	3.5	2.4

The ratio SiO_2/Al_2O_3 of three columns are in agreement with the data of the literature (Duchaufour, 1974) admits that this ratio varies between 2 and 5.5.

The results of the chemical analysis of the sodium montmorillonite MMT-Na, and the catalyst of montmorillonite deck load to the aluminium "MMT-Al", presented in the Table (1) show that the activation of the montmrillonite of the MMT before the decking with the metallic oxides (MgO, FeO₃, CaO, ...) are decreased about 30 % compared to the second catalyst (15 %).

It was noted an increase in the content of aluminium of the order of 4 % for the MMT-Al

which comes from the decking and aluminium has been decreased about 2 % for the MMT-H-Al, it results in the partial modification of the structure of the motmorillonite. It is necessary to note that this reduction of the aluminium changed the crystal shape to octahedral that left the system with negative charge and would be immediately compensated by H^+ ion according to the hypothesis of Thomas (Thomas, 1950) which confers the acidic character of clays by activation.

Besides, a clean reduction of the composition in Na_2O in relation to the MMT sample is observed with a rate of 80 %, it shows that the sodium is easily exchangeable.

Catalyst	d (Å)	Specific Surface $(m^2.g^{-1})$ —	Volume of pores (cm ³ /g)	
		Specific Surface (III.g)	V _{total}	V _{micropore}
MMT-Al (conventional)	17.86	220	0.153	0.088
MMT-H-Al (conventional)	18.22	245	0.175	0.066
MMT-Al (microwave)	17.36	260	0.183	0.093
MMT-H-Al (microwave)	18.03	270	0.189	0.082

Table (2): Properties of the montmorillonite deck load samples calcinated by classical and microwave heating

The synthesized samples develop openings of leaflets whose values are located in a region often met in the strong microporous and that vary from 16-19 Å that agrees with a height of pillars of the order of 6.5 to 9.5 Å. Reviewing that the montmorillonite of Maghnia after purification and drying, the clay has a reticular distance between 12,5-13 Å (Belaroui, *et.al.*, 2004). When it is calcinated decreases to 9.7 Å. This value corresponds to the thickness of the leaflet 2:1 (Tzou, 1983).

In the case of the interfoliated by the aluminium, the expansion of leaflets on the clay was in the range of 8 Å when the sample is calculated by classic method or by microwave to 500 °C. This rising corresponds approximately to the thickness of the aluminium polycation containing 13 atoms and of formula $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Pu, *et.al.*, 1991).

We explain this phenomenon by the following manner: the interfolaited of thick pillars of metallic oxides between leaflets of the clay is achieved to their adsorption by cataionic exchange opposite to the purified clay (MMT-Na) which showed the maximum selectivity. The reduce of this interfolar distance after calcinations results of the pillar contraction during their transformation in oxide and it is the mode of microwave heating that give a great difference of pillar contraction.

The fact is that the calcination by microwave heating occurs from the inside toward the out side of the matrix. The Al_{13} polycation changes under metallic oxide pillar shape and it self contract after the disappearance of water between leaflets.

It is true that the sample inserted to the aluminium presents a distant basalt of the order of 17.8 Å comparable to references. This distance is even bigger and it is increased of the order of 0.5 Å for our samples when the montmorillonite of departure under goes activation before the insertion.

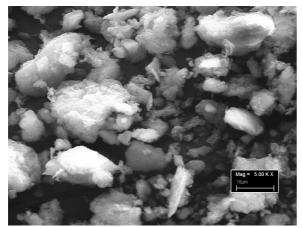
Texturale measures of these four matrixes show that the decking of the montmorillonite by the metallic polycations creates very important microporous. Compared to the specific surfaces of departure product (sodium montmorillonite) of the order of 80 m²/g (Belkhadem, *et.al.*, 2006). It leads to opening the pores and increasing of the specific surface area more than $200 \text{ m}^2.\text{g}^{-1}$ even after calcinations at high temperatures. These results indicate, the reality of the insertion, in perfect agreement with the obtained results of XRD.

Sample decked to the aluminium that prepared from the acidic montmorillonite MMT-H presents a weaker microporous compared with that obtained from sodium montmorillonite (MMT). The thermal effect of microwave was noted that values of textural measures are more important, there fore a better quality of decking occured with a gain of 24 time calcinations. Zeolites HY and ZSM-5 have sizes of microporous respectively of 7.4 Å and 5.6 Å (Breck, 1984).

In our case we find from the model of Horvath-Kawazoe, a 5.8 Å and 6.6 Å respectively for the MMT-Al and MMT-H-Al. The middle diameters of pores obtained from this model can be compared with distances interfoliaires obtained by XRD after subtraction of thickness of the leaflet of the montmorillonite that is 9.6 Å (6.4 Å for the MMT-Al and 7.1 Å for the MMT-H-Al). The two techniques drive practically to the same values of the middle size of microporous. Knowing that the model of Horvath-Kawazoe measures the accessibility to the micropore: it can be perpendicular to leaflets but is perpendicular to pillars.

It suggests that in the case of the decking by the aluminium, the distribution of pillars is distributed regularly between leaflets and the clay. Photographs gotten with the help of the scanning electron microscope picture (1) and (2) show a picture of the morphology of the structure in leaflets of clays. The analysis permits to put in evidence the presence of metallic polycations but not to distinguish them.

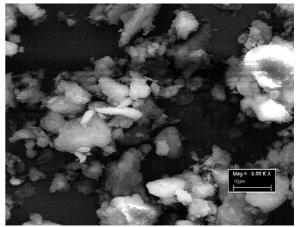
We note the distribution at random aggregations. There is no apparent porosity even relate to high magnifying. However, it is important to note that the weak pressures required by the MEB technique can modify some of the morphology of the material (loss of structure water).



Picture (1): MMT-Al

3.2. Catalytict performance of the isomerisation of the m-xylene with catalysts on the base of montmorillonite prepared conventionally and by microwave.

Figure (2) shows the effect of the variation of temperature on the isomerisation of the mxylene on the global conversion rate of the reaction for the fourth catalysts. Rates of conversions increase with the increase of the



Picture (2): MMT-H-Al

temperature for the four catalyst conventionally prepared or by microwave. A threshold of conversion is reached at 350 °C. This temperature will be taken in account as temperature of work for the remainder of the study. We note an improvement of the conversion opposite the catalyst prepared by treatment microwave and by acidic treatment.

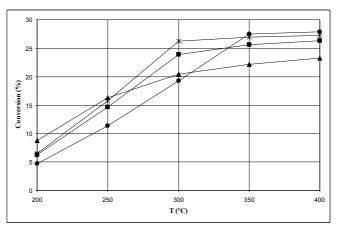


Figure (2): Effect of temperature on the rate of conversion of isomerisation of xylene.

Concerning the effect of the temperature on the results of products of reaction of isomerisation of m-xylene they increase with the increase of the temperature and especially for the para isomer as shows in Figure (3).

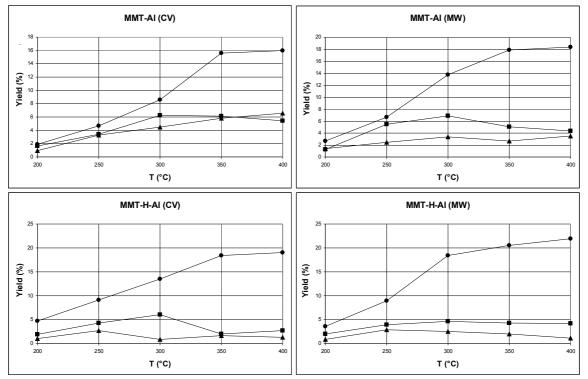


Figure (3): Effect of temperature on the results of products of the reaction of isomerisation of *m*-xylene.

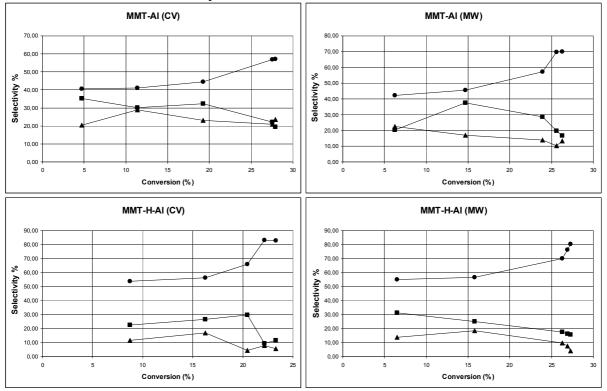


Figure (4): Selectivity according to the conversion at 350 °C

Figure 4 shows products obtained at the time of the transformation of m-xylene. The obtained products are mainly p-xylene and o-xylene as well as toluene and isomer of the trimethylbenzene. The presence of toluene and

trimethylbenzene in small quantity in the products indicates that in addition of isomerisation reaction, there is reaction of dismutation. The last requires reaction conditions of very strong acidity and a higher temperature to have the high outputs (Kirk, 1998). Whereas isomerisation requires a moderate acidity (Martens, *et.al.*, 1997). The weak values of percentage of dismutation products confirm dimensions of the average pores of the montmorillonite inserted in the sodiumic aluminium that are active for the two modes of calcinations.

The ratio p/o doesn't depend on the strength of the acid sites of the modified montmorillonite matrix it provides an information concerning the path of product diffusion.

This path depends on the porosity of the catalyst. In a general manner the value of ratio p/o permit to make the distribution between

zeolites to large pore (value near to 1) and zeolites to intermediate pores (elevation value). However, the dismutation reaction of m-xylene that leads to the formation of the toluene and trimethylbenzene requires more space around the active site (Laforge, *et.al.*, 2003).

3.3. Followed reaction of isomerisation of *the m* -xylene assisted by microwave

The reaction of isomerisation of m-xylene showed to be also a good model of reaction as a goal to determine if the heating by microwave could mislead a non conventional activation. This reaction, represented in Figure (5) consists heating of the xylene in gas phase.

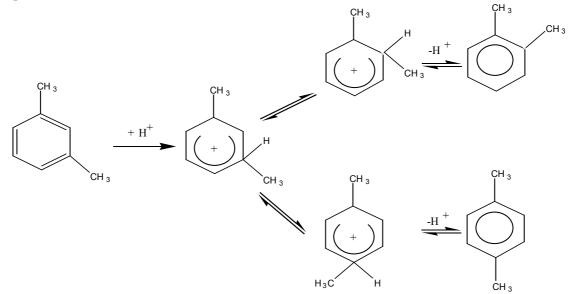


Figure (5): Reaction scheme of *m*-xylene isomerisation.

The choice of the isomerisation as a mode of reaction is due to different reasons:

1. It is a simple reaction takes place in one step, which is carried out in dry medium without use of solvent (which avoids the interactions of the latter with the microwaves).

2. This reaction implies nonpolar compounds and the ionic intermediates. Thus, one can expect strong interactions with the electromagnetic field, and a fast heating.

3. Some intermediates of the reaction are ionic species; the ionic relaxation is known by its significant processes of interaction with the microwaves, which could possibly have consequences on the course of the reaction with microwaves.

3.2.1. Comparative kinetic study between the microwave heating and the conventional heating

3.2.1.1. Order of reaction

Generally, the transformation of the *m*-xylene gives a mixture of para and ortho xylenes, therefore the reaction can be schematised in a simplified way as follows:

$m \rightarrow p + o$

m is meta xylene,

p is para xylene,

o is ortho xylene.

The expression of the speed reaction of isomerization v is written:

 $\mathbf{v} = \mathbf{k} [\mathbf{m}]^{\sqcup}$

Where: α is the order of the reaction,

k is the rate constant

[m] is the concentration of the meta xylene.

The previous equation can be rewritten as follows:

 $\ln(v) = \ln(k) + \Box \ln([m])$

For the 1st order reaction we can write:

 $\ln (1$ -Conversion) = -k.t

If we draw the curve of ln (1-Conversion) according to time, we must get straight line with a slope of (-K) in the case of 1^{st} order reaction.

The orders of the reaction of isomerisation for the conventional heating and the irradiation microwaves have been given by studying the kinetics of the reaction. We found that the order of the reaction is 1 for the conventional heating as well as for the microwaves. These results were the best in agreement with the kinetic data that we obtained. Thus, this isomerisation is a first order reaction for the conventional heating as well as for microwaves. The heating system did not influence the mechanism or the advance of the reaction.

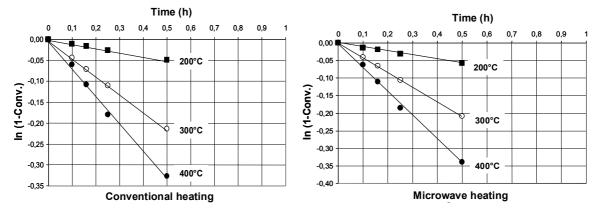


Figure (6): Experimental determination of the order of the isomerisation reaction for the conventional heating and microwaves.

3.2.1.2. Energy of activation

The energy of activation is determined experimentally by the realisation of the reaction at different temperatures, and by using the equation of Arrhenius data as follow:

 $k = A \exp(-E/RT)$

A is the pre-exponential factor,

E_A is the activation energy, J/mol,

R is the constant of the ideal gases = 8.314 J/mol.°K

T is temperature °K.

By taking the logarithm of the above equation we get:

 $\ln k = \ln A - E/RT$

we can easily see that the tracing of the variation of the ln K according to $\frac{1}{T}$ represents a straight line, whose slope is proportional to the activation energy.

The kinetic parameters of the reaction of isomerisation have been determined under atmospheric pressure by carrying out a series of experiments at certain temperatures (200 °C, 300

°C, 400 °C) under the two modes of heating, classic and microwaves. Thus, we could determine the kinetic constants k of the reaction at various temperatures for the two modes of heating. These rate constants have been deduced starting from the data of figure 6, representing the slope of the straight line ln (1-C) against time.

As Figure (7) shows, the kinetic data follow the law of Arrhenius perfectly, K (T) = A exp (-Ea/RT), for the two modes of heating. The energy of activation of isomerisation and the factor pre-exponential can be directly deduced:

Ea (microwaves) = $26 \pm 2 \text{ kJ}$ / mole Ea (heating conv.) = $27 \pm 2 \text{ kJ/mole}$ A (microwaves) = $89.\text{h}^{-1}$

A (heating conv.) = $100.h^{-1}$

These results show that there is no kinetic effect of the microwaves: by taking in account the experimental errors, the values of the rate constants and activation energy are in the same order in both modes of heating.

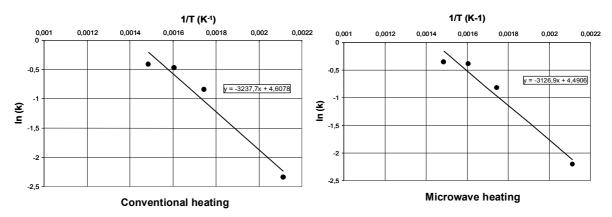


Figure (7): Experimental determination of the activation energy of the reaction of isomerisation of conventional heating and microwaves.

3.2.2. Influence of the nature of the heating on the conversion and selectivity

The kinetic aspects of the reaction form only one part of the chemical process: conversions and the selectivity are also significant in the establishment of the matter assessment of the process. For that, we studied the influence of the temperature of work on the conversion and selectivity of the reaction of isomerisation of *m*-xylene under the two modes of heating. The reaction was studied in a range of temperature varying from 200 °C to 400 °C, for a constant VVH. The results are presented in Figure (8) for conversions and on Figure (9) for the selectivity.

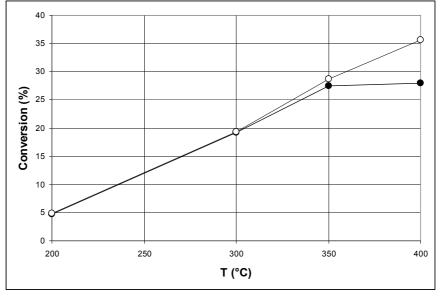


Figure (8): Influence of the nature of heating on the reaction of isomerisation

• conventional heating • heating microwaves.

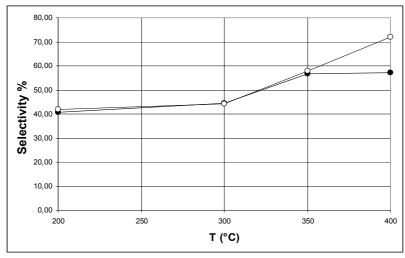


Figure (9): Influence of the temperature on the selectivity of isomerisation
conventional heating or microwaves heating

The conversion optimum of m-xylene and selectivity of p - xylene under conventional heating are observed around a temperature of 350 °C. Below this optimum, there is no significant difference between conventional heating and microwave had been observed. On the other hand, at higher temperatures, better results are clearly obtained by using the microwaves:

- The conversion under microwaves heating is proportional directly with temperature increasing whereas under conventional heating it reaches a limit.

- The selectivity of *p*-xylene increases under microwaves heating, whereas under conventional heating, it arrive a limit.

These differences between the two modes of heating are due to the nature of their mode of transfer of heat. In the laboratories and industry, the heating by conduction or convection (called traditional or conventional heating) is often used for the implementation of reactions. The transfer of heat to the heated medium is sometimes limited by the efficiency of the thermal transfer of the walls of the container as well as catalysts. For the heating by microwaves, its principle is based on the direct absorption of energy by the reagent and the catalyst which warm up directly; the transfers of heat are then reversed compared to the heating by conduction or convection. On the contrary, the microwaves allow the heat in the mass.

Finally, it is necessary to notice that this study of the influence of the temperature on the reaction of isomerisation under the two modes of heating, also related the influence of the power of microwaves on the products of reaction. The temperature of the system under microwaves is a function of the power incidental microwave.

4. Conclusion

The Preparation of four catalysts for isomerisation of *m*-xylene starting from clays by the polycation of aluminium hydroxide permitted to prepare a structure of acid microporous: two catalysts MMT-H-Al and two MMT-Al treated by conventional calcination and microwaves. The characterization by various of physicochemical analyses methods showed that there was not a great difference of structure, specific surface or basalt distance. The microwaves treatment made it possible to reduce the duration of calcination (to 10 min.) while the duration of calcinations by conventional heating is (5 h). The four catalysts have been tested for the reaction of isomerisation of *m*-xylene. The results showed a great selectivity of isomerisation compared to the reaction of dismutation. Which make the catalyst prepared from gravitational decked clay very important due to its capacity of conversion and for its selectivity into p - xy lene.

The question about the existence of an effect of specific non thermal activation of the microwaves was widly discussed during last year. In case of our reaction of isomerisation, the answer is clearly negative. This conclusion is in agreement with the weak energies which the microwaves can transmit. Activation could take place only by one accumulation of energy in the system, which would give place to zones of high energy or a high state of activation; this theory is also excluded because the relieving of the molecules subjected to a field microwaves is too fast to allow such phenomenon. However, certain results of the literature and our study let us to suppose the existence of non traditional heating effects non classic resembling on activation.

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الخلاصة

إن تحضير وتشخيص التركيب للطين الجزائري المسمى Montmorillonite المحتوي على الألمنيوم بين طياته، كشف بأن التكلس بواسطة تسخينه في فرن المايكرويف يتم في عشرة دقائق فقط. هذه النتائج تبين التطابق التام بين هذا التركيب والتركيب المحصل عليه بواسطة التسخين التقليدي بالفرن العادي (خمسة ساعات).

تبين القياسات المختبرية لأربعة أنواع من الأطيان بإن إدخال المعادن متعددة الأيونات الموجبة في هذه الأطيان تخلق نظام مهم ذات المسامات الدقيقة. إن الصفات التحفيزية لهذه المادة الصلبة ذات المسمات الدقيقة تم استخدامها لتحويل ميتا-زايلين كتفاعل نموذجي والتي تبين الإنتقائية العالية لأزمرة ميتا-زايلين إلى أورثو وبارا-زايلين.

بوخته

ئاماده کرن و تەرخانکرنا پیکھاتا ئەلەمنىيومى داپوشى ب جورە کى ئاخى ل جەزائىيرى (Montmorillonite) ديار دكەت كو ئەف ئاخە ب دەھ دەقىقان دەردكە قىت دەايكروي شى دا (Microwave) بدوماھىك دھىت . دەرئەنجامى تەرخانكرى يى بەريكىن دى يا ژھەمى يا نىيزىكتر پىيىنج (Microwave) بدوماھىك دھىت . دەرئەنجامى تەرخانكرى يى بەريكىن دى يا ژھەمى يا نىيزىكتر پىيىنج (Montmorillonite) بدوماھىك دھىت . دەرئەنجامى تەرخانكرى يى بەريكىن دى يا ژھەمى يا نىيزىكتر پىيىنج (Microwave) بدوماھىك دھىت . دەرئەنجامى تەرخانكرى يى بەريكىن دى يا ژھەمى يا نىيزىكتر پىيىنج (Montmorillonite) بدوماھىك دھىت . دەرئەنجامى تەرخانكرى يى بەريكىن دى يا ۋھەمى يا نىيزىكتر پىيىنج (Montmorillonite) بىرە. پىشان قان چوار نىموونان وەسا دىار دكەن روويى قى ئاخى (Polycations) سىستەمى كونىت گەلەك بېرويىك چىدكەت ب رىكا كانزايىن گەلەك كاتەيون Rayo) بىرە ھەيى . رەرە سىتىن ھەيى . رەرە سىيىتەمى كونىت گەلەك بېرويىك (Micro porous) بىرە ھەيى . يىن ھەيى . رەرە سىيىتە ھەين . دەرەشتىيىن ھاريكار يىيىن ئەقان كونىن گەلەك بېرويىك (مەرە بىيىن ھەيى . دەرەشتىيىن ھاريكار يىيىن ئەقان كونىن گەلەك بېرويىك (مەرە بىيىن ھەيى . يەرە بىيىن ھەرىيا ھەيى . دەرە بىرەرىيى قىزىكەكەت بېرويىك يەرە يەرە يىن گەرەك كاتەيون دەرە بېرەرىيە . يەرەرىيى ھەيى . يەرە يەرە يەرەرىيى ھەيى . يەرەرىيى ھەرىيا . يىيىن ئەقان كونىيىن گەلەك بېرويىك (Bicro porous) بىز گەررىيا . يەرەرىيا . يەرەرىيا . يەرە يەرەرىيە . يەرەرىيى قىزىكەكەكا تاقىگەر، ئەۋا ھەنى ئەنجامەكى ناياب بەمستخوقە دىيىيت لىرىيكەكا تاقىگەر، ئەۋا ھەنى ئەنجامەكى ناياب بەمستخوقە دىيىيت لىرىكەكا تاقىگەر، ئەۋا ھەنى ئەنجامەكى ناياب بەمستخوقە دىيىيى لىرىكەكا تاقىگەر، ئەۋا ھەنى ئەنچامەكى ناياب بەمستخوقە دىيىيە لىرىكەكا تاقىيكەر . يەرەلىكەكا تاقىگەر، ئەۋا ھەنى ئەنجامەكى ناياب بەمستخوقە دىيىيە دىيىت كەرلىكە . يەركەكا تاقىگەر، ئەۋا ھەنى ئەنجامەكى ناياب بەمستخوقە دىيىيە يەلەيكەكا دەركەكەكا تاقىكەر . يەرەلىكەكە يەيە . دەرەلىيىكە يەركەكەكە يەرەلەكە . يەرەلىكەكە يەرەلەپ يەرەلەپ يەلەپ يەرەپ يەرەپ . يەرەلەپ يەرەپ يەرەپ يەپ يەرەپ ي