Synthesis, characterization and catalytic evaluation of zirconia-pillared bentonite for 1, 3-dioxalane synthesis

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The aim of this work is to study the solids obtained by pillaring Tunisian bentonite with zirconium polycations from the hydrolysis of zirconium tetrachloride. For comparative purposes, the pillaring of Wyoming montmorillonite, a reference clay, is also studied. Variations in the dialysis number, concentration of Zr solution, pH, temperature in the synthesis procedure as well as the pillaring method, affect the structure and properties of the pillared clay obtained. It has been verified that the structure of the pillared clays strongly depends on the method of preparation and the pH Zr solution in some cases, well ordered pillared clays (with basal spacings between 15 and 18.2A) have been obtained, while in several others noncrystalline solids yielded. Delamination of the clays seems to take place both when the intercalation solutions obtained from zirconium tetrachloride have pH > 2.8 and when they are subjected to a reflux treatment. Best results were obtained at pH = 2.8 $[Zr^{4+}]$ = 0.1M, at room temperature, and when using five dialysis, the direct method. The specific total surface area and micropore volume of the solids have reached the values up to 200 $m^2\ g^{-1}$ and 0.06 $cm^3\ g^{-1}$, respectively. Potentiometric titration and mass titration data suggest that pillared materials produce a shift of the point zero charge toward the point zero charge of the zirconium oxide. The amount of ZrO_2 fixed have varied between 6 and 30% of the weight of the pillared samples. The activity of the zirconium pillared clay for 1,3-dioxolane synthesis has been investigated. The method of intercalation has been found to be the most suitable for this reaction.

Keywords: Zr-oligomer; pillared clay; point of zero charge; 1,3-dioxolane; acetalization.

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INTRODUCTION

Pillared interlayered clays (PILCs) include a new family of clays based on two-dimensional materials, and are used in adsorption and catalysis. Pillaring of clay with inorganic polycation results in producing thermally stable rigid cross linked materials with a large surface area, a certain porous texture and acidity. The properties of pillared clays depend upon several factors such as the preparation conditions (mainly pH and temperature) of the polycations, the method of intercalation, washing and drying steps. Among the cations utilized for pillaring, one of the most extensively used up to date is a polynuclear hydroxy zirconium complex whose structure is $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$ [1, 2]. The most commonly studied is the zirconium intercalated clay using $ZrOCl_2$, $8H_2O$ as a precursor [1–6]. Several works using zirconium acetate [7–10] are included in the literature list, but up to now, only one paper describing the pillaring with zirconium oligomers using $ZrCl_4$ as a source of zirconium species has been published [11], to the best of the authors' knowledge.

The aim of the present work is two-fold: first, to study the solids obtained by pillaring Tunisian bentonite with zirconium polycations using $ZrCl_4$ as a precursor. In other words, under investigation are the effects of the initial concentration of $ZrCl_4$, the pH of the pillaring solution, its temperature, washing and the pillaring method applied on the structural and textural properties of Zr pillared Tunisian bentonite. Then, the application of the pillared bentonite as a catalyst in the synthesis of 1,3-dioxalane using acetone and et-hylene glycol is also investigated. For comparative purposes, the pillaring of Wyoming montmorillonite, a reference clay, is also studied.

In recent years, considerable attention has been paid to the synthesis of 1,3-dioxalane. Thanks to its properties (having no unpleasant odor, being miscible in water and the majority of organic solvent, not toxic), this molecule is used as a reagent mainly for the protection of the carbonyl group or solvent in several applications: in organic chemistry [12, 13], in polymer [14], pharmaceutical [15–17] and biological [18, 19] industries.

The synthesis of 1, 3-dioxolane is generally catalysed by homogeneous acid catalysts such as Rhodium (II) acetate [20], p-toluenesulfonic acid [21], tin (II) chloride [22] and manganese (III) acetate [23]. In addition, it is prepared in the presence of a solvent like acetone [22, 24], or $CHCl_2$[20], ACOH, MeCN, Me_2CO, MeOH, $CHCl_3$ [23]. Unfortunately, these catalysts cause corrosion and are not environmentally friendly.

On the contrary heterogeneous catalysts based on pillared clays have many advantages. They are noncorrosive and environmentally friendly. Their re-

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peated use is possible and their separation from liquid products is easier compared to homogeneous catalysts.

The originality of our investigation is the purpose to synthesize 1,3-dioxolane using acetone and ethylene glycol catalyzed by zirconium pillared clays without any solvent.

EXPEREMENTAL

Starting Materials

Two natural clays were used in this work. A bentonite (G) from Gafsa, southwest of Tunisia, and a well-known montmorillonite (W), a clay from Wyoming, the USA. In order to prepare pillared materials, those two clays were purified by conventional sedimentation, exchanged with a 1 M solution of NaCl. According to the X-ray diffraction (XRD) study results presented in Fig. 1, the comparison between diffractograms of crude and purified clays shows the presence of quartz (d_{001} = = 3.35Å) and calcite (3.03Å) as impurities in G and quartz (d_{001} = 3.35 Å) and of feldspar (d_{001} = 3.18 Å) in W clay. In the case of G bentonite, in order to eliminate the calcite (23%), the sample was firstly treated with HCl 0.3M before purification.

Table 1. Chemical compositions of G and W purified clays expressed in the oxide form/100g of the calcined sample

	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	MgO	CaO	K_2O
Na-G	61.38	24.80	8.03	3.06	1.38	0.13	1.40
Na-W	66.25	23.33	3.85	3.14	2.91	0.14	0.15

Table 2. Physico-chemical properties of G and W purified clays

	S_{BET} (m^2/g)	S_{ext} (m^2/g)	$S_{\mu p}$ (m^2/g)	V_p (cm^3/g)	$V_{\mu p}$ (cm^3/g)	CEC
G	29.2	29.2	0	0.08	0	31
Na-G	107.2	67.5	39.7	0.15	0.02	78
W	27	27	0	0.12	0	90
Na-W	112	59.7	52.3	0.15	0.02	98

The shift of 001 peak from 2θ = 7.30° (d_{001} = 12 Å) to 2θ = 5.18° (d_{001} = 17 Å) when treated with glycerol and to 2θ = 8.84° (d_{001} = 9.9 Å) when heated at 500°C, indicates the presence of the smectite fraction. The appearance of 002 peak at 2θ = 9.95° (d_{001} = 8.83Å) shows that G clay is an interstratified illite/smectite, according to [25], whereas in the case of *W* clay this peak appears at 2θ = 10.28° (d_{001} = 8.46Å) signifying that the American sample is a montmorillonite. Reflections at 2θ = 12.39° and 2θ = 24.92° (7.13 and 3.56A°), which disappear after heating at 500°C, show the presence of a small amount of kaolinite in G bentonite. According to the chemical composition given in Table 1, the structural formulas of Na-G and Na-W were found to be: $[Si_{7.43}\ Al_{0.57}]\ [Al_{2.96}\ Fe_{0.73}\ Mg_{0.24}]\ O_{20}\ (OH)_4\ Na_{0.71}\ K_{0.21}\ Ca_{0.01}$ and $[Si_{7.84};\ Al_{0.15}]\ [Al_{3.10};\ Fe_{0.34}\ Mg_{0.51}]\ O_{20}\ (OH)_4\ Na_{0.72}\ K_{0.02}\ Ca_{0.01}$, respectively. Physico-chemical properties of G and W clays before and after purification are illustrated in Table 2. As can be seen, the two Na-bentonites have a comparable specific surface area (107 and 112 m^2g^{-1}) but the cationic exchange capacity (CEC) of the Na-G clay is lower than that of Na-W: 78 and 98 meq/100 g, respectively. Lower CEC is due to the presence of illite and kaolinite which are not swelling fractions.

Preparation of Pillaring Solutions

Zirconium intercalating solutions were obtained by slow adding of 0.2M NaOH solution to zirconium tetrachloride $ZrCl_4$ under vigorous stirring and using different values of pH: 1.8; 2.5; 2.8 and 3.3. Three initial concentrations of Zr were used: 0.01, 0.1 and 0.5 M. In the present work the pillaring solution was prepared at room temperature and under reflux. The obtained solution was aged under stirring at room temperature for 24 h. The preparation of Zr pillared interlayered clay by the method of heating under reflux using zirconyl chloride ($ZrOCl_2$, $8H_2O$) [5, 26, 27] and zirconium acetate was extensively studied [7, 28] but, to the best of our knowledge, the hydrolysis under reflux conditions of $ZrCl_4$ as the source of polycations has not been reported so far.

Synthesis of the Zr Pillared Clays

Two methods (the first of them in two variants) were used to prepare the intercalated samples (Fig. 2):

- A classical method, called 'D', where the pillaring solution is slowly added to the clay suspension (1 g/100 ml). When the solution, previously refluxed, is added dropwise to the clay suspension, the method is called 'DR'.
- An inverted method to the previous one called 'I' where the dry clay powder (1 g) is directly dispersed in the pillaring solution (100 ml). This second method decreases the amount of liquid manipulations and the time of the process. It leads to a better ability of powdering of the final pillared dried product.

The intercalation reaction was performed with both methods using Zr/clay ratio of 10 mmol/g. The mixture was aged for 24h under stirring. After that, the resulting products were separated from suspension by centrifugation, washed by dialysis with distilled water, dried at 350 K and finally calcined for 2 h at 823 K.

The Zr PILCs are labeled as following:

$$\textit{bentonite} - \textit{method}^{\mathrm{pH}}_{\left[\mathrm{Zr}^{4+}\right]i}$$

Catalytic Study

The acetalization reaction of 7.68 g (124 mmol) of ethylene glycol and 3.64 g (63 mmol) of acetone

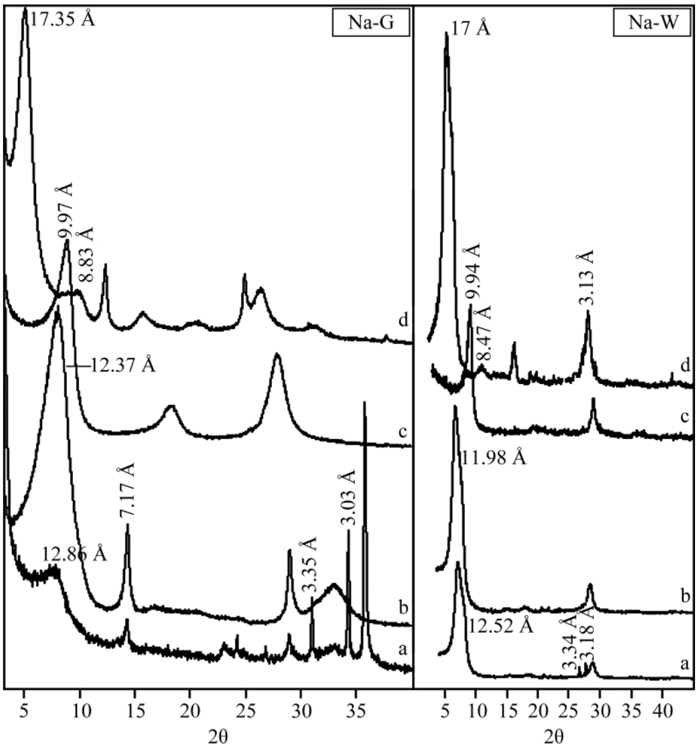


Fig. 1. XRD pattern of oriented films. (a) crude; (b) purified; (c) heated at 500°C and (d) glycerolated.

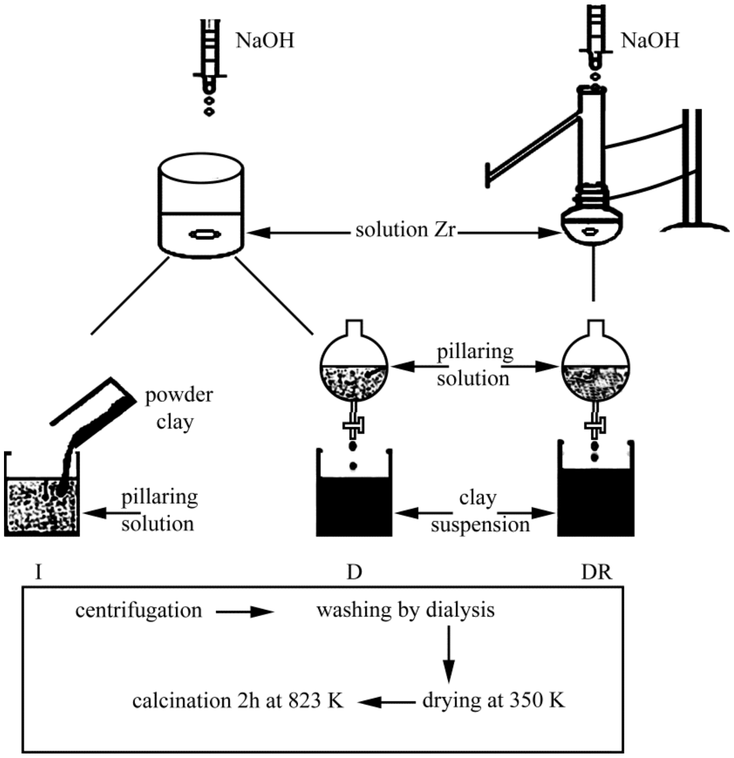


Fig. 2. Illustration of different pillaring methods D, I and DR.

in the presence of 0.1 g of PILCs was carried out in the autoclave (100 cm^3) at 40°C under autogenous pressure and without solvent. Then, the reaction mixture was cooled and filtered to separate the clay catalyst. To recuperate the 2,2-dimethyl-1,3-dioxolane, the filtrate was treated with 20 ml of distilled water (3 times) to eliminate the residual ethylene glycol. The organic phase was extracted with diethyl ether. After evaporation of the solvent (ether and acetone), the product was identified by its ^{1}H NMR spectral analysis.

Characterization methods

The XRD technique was carried out with a 'Panalylitical X'Pert HighScore Plus' device, which operates with Cu Kα radiation.

N_2 adsorption–desorption experiments were carried out at 77 K on (Autosorb I) Quantachrome Instruments. The N_2 isotherms were used to determine the specific surface areas (SA) using the BET equation. The micropore volume was determined using the t-plot method and the total pore volume of the samples, Vt was calculated at $P/P_0 = 0.99$. Before each measurement the samples were outgassed for 2 h at 130 °C.

The chemical composition of both the starting material and the modified samples was determined by atomic adsorption with the spectrometer of the type AAS Vario.

Cation exchange capacity (CEC) was determined by the Kjeldhal method. Several samples of 200 mg each were exchanged with the ammonium acetate (1 M) three times and then washed with anhydrous methanol, with the final washing with deionized water performed three times. The amount of ammonium retained was determined using a unit of Kjeldhal. The CEC is expressed as a mili-equivalent per 100 gram of the calcined sample.

Potentiometric titration measurements were performed at a Titrando 716 automatic titrator (Metrohm) at ambient temperature and aerated medium. For all the acid–base titrations, a certain amount of 0.1 g of clay was added to a 15 ml water flask. The suspension was firstly acidified by HCl 10^{-2} M at pH of about 3. NaCl solution was used to stabilize the system at a fixed ionic strength (0.1, 0.01, and 0.001 mol l^{-1}). Distilled water was added to increase the total initial volume of the suspension to 50 ml. The mixture was stirred overnight in order to attain equilibrium. Afterwards, 5×10^{-2} M NaOH was used to titrate the suspension up to a pH of about 12. Considering the blank system for each sample, we have used the same mixture without clay. The point of zero charge (PZC) value and acid center were determined according to the method described in [29] using the proton adsorption or proton charge σ_H (mol/m^2) with the following formula:

$$\sigma_H\left(\mathrm{mol/m^2}\right)=\frac{V}{m}*S\left(\left[H^+\right]_b-\left[H^+\right]_s\right)-K_W\left(\frac{1}{\left[H^+\right]_b}-\frac{1}{\left[H^+\right]_s}\right)\Bigg\} \qquad (1)$$

Here, V is the volume of the electrolyte solution equilibrated with clay (50 ml), [H^+] is the proton concentration in the solution (molL^{-1}), K_W is the dissociation product of water (10^{-14}), subscripts ‘s’ and ‘b’ refer to the sample and blank solutions, m is the mass of the sample used (0.05g), and S is the specific surface area (m^2/g).

Applying the methods described in literature [29], under similar conditions **mass titration experiments** were performed of the potentiometric titration followed by the pH drift until a steady value was achieved. Each portion of 0.05 g of a dry clay sample was added to 50 ml of NaCl solution at different ionic strength with the pH between 3 and 10. After each addition, the pH was recorded after an “equilibrium time” of about 15 min. Then a new amount of the sample was introduced to make changes in the pH. This procedure was repeated until no pH change occurred.

Surface acidity (Brönsted and Lewis acid centers) was determined by the FT-IR spectroscopy on the basis of adsorption of Butylamine. With this method, 10 ml of the prepared Butylamine in the cyclohexane solution was added to 0.1 g of catalyst. The mixture was shaken at room temperature. After drying, each sample of dry clay was calcined at different temperatures. FT-IR spectra were recorded under evacuation in the region of 1800–400 cm^{-1} on a Perkin-Elmer infrared Fourier transform spectrometer using the KBr pellet technique.

^{1}HNMR study was used to determine the catalytic reaction yield. Different spectra were recorded at 300MHz on a Bruker AM 300 spectrometer using spinning samples tubes with a 5-mm external diameter. Temperature was fixed at 25°C using a Bruker VT 1000 variable temperature control unit, measured by calibrated Pt-100 resistance thermometer. The chemical shifts are given in ppm with respect to external TMS reference at 0 ppm.

RESULTS AND DISCUSSION

Influence of preparation parameters

The dialysis number, temperature, initial concentration and pH are key factors in controlling the nature of the zirconium species present in the solution, which are responsible for the intercalation process. The determination of conditions was carried out mostly on the Tunisian G bentonite. The effect of a pillaring method is also studied, using the W clay was used as a reference sample for comparative purposes.

The effect of dialysis number

The intercalated clays were separated by centrifugation and washed by dialysis at the ratio of 2L of water per 1g of clay. During this process, small quantities of clay were extracted, calcined at 823K and analyzed by XRD. Figure 3 illustrates an example of diffractograms of G_D sample both without washing and at different stages of washing. The X-ray data show that prior to washing the solid is totally delaminated and after a number of washing procedures there is a progressive definition of the 001 line until five dialysis (d_{001} = 17.3Å). After that the intensity decreases from 17.3 Å to 15.87 Å and the peak becomes broader when the clay is dialyzed 8 times. This change could indicate that the arran-

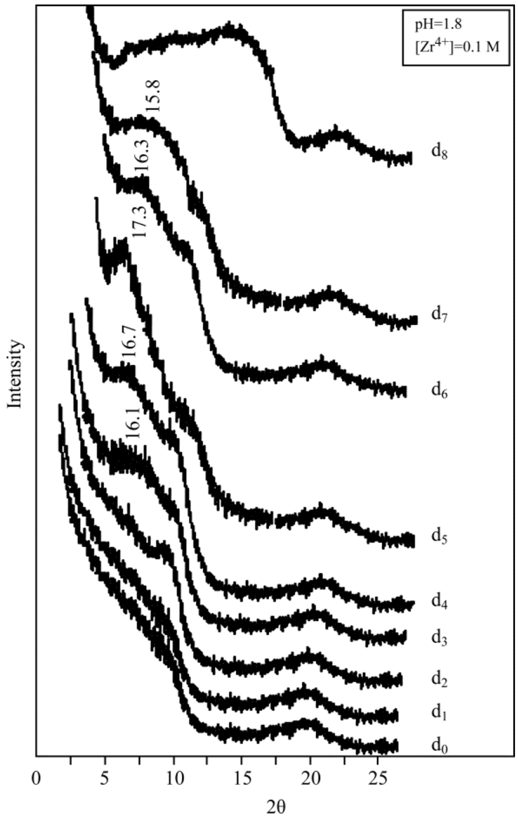


Fig. 3. X-ray diffractograms of $G-D_{0.1}^{1.8}$ sample before and after 1 to 8 dialysis.

gement of the intercalated structure in the interlamellar space ends during washing. So the dialysis stage has a beneficial effect on the crystallinity and Zr polymerization of products but an excessive washing leads to a delamination of the product. The positions of the 001 peak correspond to interlayer distances (d_{001}) of about 17 Å after intercalation with zirconium species; this value can be compared to the 12.4 Å of the starting material, showing that samples were intercalated. Nevertheless, the intensity and broadness of the 00l diffraction peaks demonstrate an inhomogeneous staking of the clay layers, typical of the zirconium PILCs.

The effect of initial Zr concentration

Fig. 4 presents the XRD patterns after calcination at 823 K obtained with different initial concentrations of Zr^{4+}. As can be seen, d_{001} increases from 15.9 to 17.7Å when Zr^{4+} concentration increases from 0.01 to 0.5M. Also when a low Zr^{4+} concentration is used, the 001 peak becomes broader and its intensity is lower, indicating a less uniform structure. The presence of a peak at 2θ around 9.9Å seems to indicate the existence of a fraction of unpillared material.

Pillared clay prepared with a 0.1M Zr^{4+} solution presents the highest micropore volume and specific surface area (see Table 3). The increase of initial Zr^{4+} concentration substantially increases the percentage of Zr introduced in the pillared sample from 6.44% to 17.33% for $G-D_{0.01}^{1.8}$ and $G-D_{0.5}^{1.8}$, respectively. It has to be noted that the Zr fixed is not exchangeable with Na^+ cation when PILCs are redispersed in NaCl (1M) solution. In theory, the value of the residual CEC, which can be used as a tool for measuring the intercalated zirconium linked to the sheet of clay, must decrease with an increase in the quantity of Zr. However, in our case, the determined values of the residual CEC do not follow the increase of the ZrO_2 percentage detected by chemical analysis. So a certain amount of Zr may be adsorbed as a neutral species such as $Zr_4(OH)_{16}$ [1] or the increase of Zr concentration may contribute to the polymerization.

The effect of pH

The oriented powder X-ray diffractograms of pillared clays prepared under different pH are shown in Fig. 5. As can be seen, the d_{001} value of the obtained peaks enhances with the rise of the pH value until pH = 2.8. When using a higher pH (pH = 3.3), the 001 reflection disappears indicating a delaminated clay structure.

The chemical analysis data in Table 4 show an increase in the Zr quantity with the pH up to 2.8. This means that the hydrolysis progression is an explicit function of the NaOH content. When using a higher pH (pH = 3.3), the Zr quantity decreases. According to the species distribution diagram in

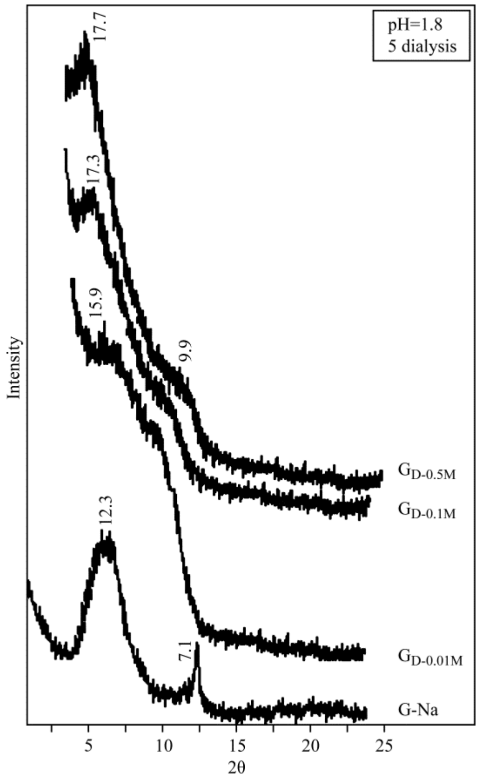


Fig. 4. X-ray diffractograms of Na-G and pillared clays.

Table 3. Textural properties, % of ZrO_2 and CEC of starting material and Zr-PILCs: effect of initial Zr content

	S_{BET} (m^2/g)	$S_{\mu p}$ (m^2/g)	V_p (cm^3/g)	$V_{\mu p}$ (cm^3/g)	CEC (meq/100 g)	ZrO_2 (%)	$^{*}ZrO_2$ (%)
Na-G	107.2	39.7	0.15	0.02	78	0	0
$G-D_{0.01}^{1.8}$	160.2	81.1	0.16	0.04	40	6.44	6.34
$G-D_{0.1}^{1.8}$	172.5	117.6	0.19	0.05	32	11.09	11.06
$G-D_{0.5}^{1.8}$	125.1	51.7	0.28	0.04	35	17.33	17.19

**: after exchange with* NaCl (1M)

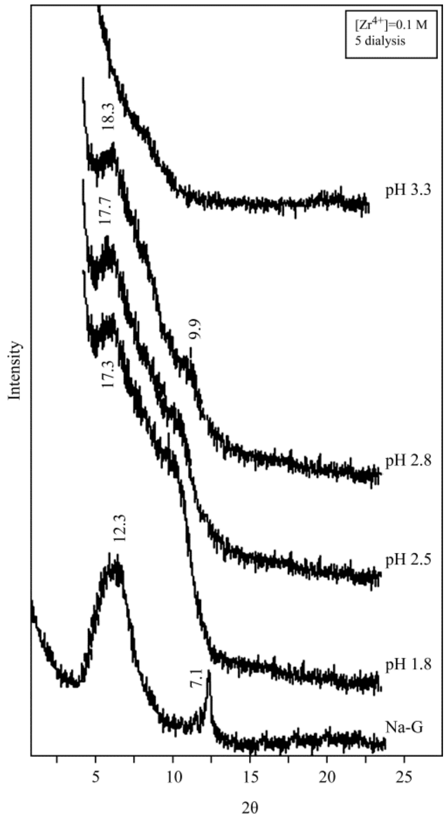


Fig. 5. X-Ray diffractograms of Na-G and $G-D_{0.1}^{pH}$ zirconium pillared clays: pH effect.

Fig. 6 obtained by [11], this behavior can be explained by the evolution of the tetramer predominant in the interval of $1.8 < pH < 3.7$. The high residual CEC for this sample (41 meq/100 g) and the decrease of the zirconium amount after its redispersion in the 1M NaCl solution (Table 4) prove the existence of a part of zirconium that is not irreversibly fixed to the structure.

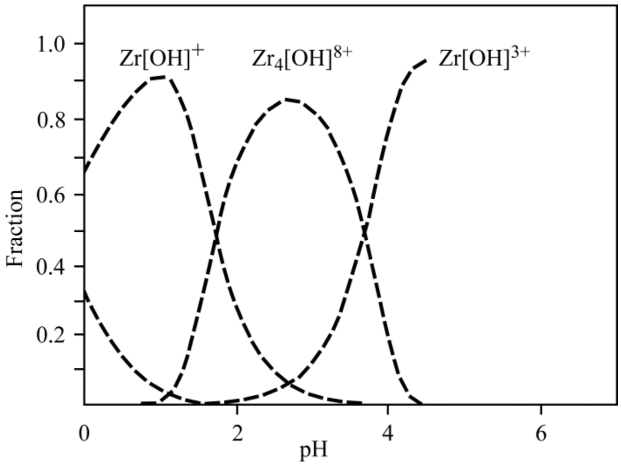


Fig. 6. Species distribution diagram for polyoxocations in aqueous solution [11].

The best results are obtained for $G-D^{2.8}_{0.1}$ sample which has the highest S_{BET} (about 200 m^2/g) and Vμp (0.063 cm^3/g) as well as the lowest CEC (24 meq/100g).

The Effect of the Pillaring Method

Physico-chemical characterization of the product obtained after pillaring the clays of Na-G and Na-W presents similar results as shown in Fig. 7. In fact, the direct (D) method leads to pillared samples with best properties: higher d_{001} (18.3Å), S_{BET} about 200 m^2/g, best V_p (0.2 cm^3/g) and lowest CEC (≈ 25 meq/100 g). Considering the intercalation of the Na-clays with zirconium polycations under the reflux conditions, it must be emphasised that this method results in the total delamination of the clay structure which becomes disordered, thus giving products on which the (001) reflection peaks disappear. Similar results have been reported in earlier studies using montmorillonite [2] and saponite [7], which explains the degradation of the clay structure by the quick drop of pH to low values of $pH < 1$. However, it should be noted that in our case, the pH of the intercalated solution remains the same ($pH = = 2.8$) irrespective of the method applied, whereas the destruction of the clay structure was detected only for the samples prepared by the DR method. In addition, the clays obtained under reflux contained higher amounts of zirconium, about 29% as ZrO_2, than the pillared clays obtained by the hydrolysis of the zirconium precursor at ambient temperature using either the D or the I method. The chemical analysis data of this solid after dispersing in the NaCl solution (1M) showed that about half of zirconium was detected in the solution of NaCl. This amount was removed by exchanged reaction, which explains the high value of CEC (≈ 47 meq/100 g) (see Table 5). As is clear from Table 5, chemical analysis shows a partial dissolution of the octahedral cation. This result is in good agreement with the IR data (Fig. 8). In fact the disappearance of the 3629 cm^{-1} (Al_2OH stretching vibration) and 913 cm^{-1} (libration bands Al_2OH cm^{-1}) peaks denotes the change in the clay structure provoked by the process. These changes must be related to the dissolution of the aluminium. Similar results are observed in [26, 30].

Surface acidity

The acidity is one of the important properties required from PILCs. It was also investigated to evaluate the application of PILCs in a commercial catalytic process. The acid-base potentiometric titration curves at different salt concentrations were used to measure the proton adsorption or proton charge σ_H (mol/m^2) which was calculated from equation (1).

An example of the curve σ_H vs. pH for Na-G and $G-D^{2.8}_{0.1}$ samples at three different ionic strengths is shown in Fig. 9. There the results reveal that, on the one hand, the surface undergoes one protonation and one deprotonation reactions in the pH range of 3–12. On the other hand, our experimental titration curves demonstrate that the studied samples in the proton adsorption curve at various ionic strengths do not show a net crossing point but a crossing domain. A similar observation was reported in earlier studies [31–34].

The intercalation of Zr species saves the slope as well as the shape of the curves and produces a shift in the pH where these curves intersect. This pH, which defined the point of zero charge (PZC), shifts from 8.6 and 7.3 for Na-G and Na-W bentonite, respectively, to about 4.7 for all pillared samples (Table 6). This value is in good agreement with the PZC value of ZrO_2 reported in literature [35].

To verify the PZC values estimated by the potentiometric method, we also determined the PZC of different samples using mass titration according to the method described by Noh and Schwartz [29]. As is shown in Fig. 9, the pH is gradually changing with the addition of a solid mineral and asymptotically approaches the limiting value. The pH thus estimated defined the PZC of the solid. The PZC values at different ionic strengths are reported in Table 6 and marked with arrows in Fig. 10. It is possible to deduce here that there is very good agreement between acid-base potentiometric titrations and mass titration. To estimate the number of acid centers we employed the method described by Sposito [36].

Table 4. Textural properties, % of ZrO_2 and CEC of starting material and Zr-PILCs: effect of pH

	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_p (cm^3/g)	$V_{\mu p}$ (cm^3/g)	CEC meq/100 g	ZrO_2 (%)	*ZrO_2 (%)
Na-G	107 .2	39.7	0.15	0 .021	78	0	0
$G-D_{0.1}^{1.8}$	172.5	86.1	0.16	0.056	32	11.09	11.06
$G-D_{0.1}^{2.5}$	189.2	123.6	0.22	0.052	26	14.05	13.99
$G-D_{0.1}^{2.8}$	199.5	122.2	0.21	0.063	24	16.71	16.54
$G-D_{0.1}^{3.3}$	174.3	96.8	0.18	0.052	41	12.54	8.68

*: *after exchange with* NaCl (1M)

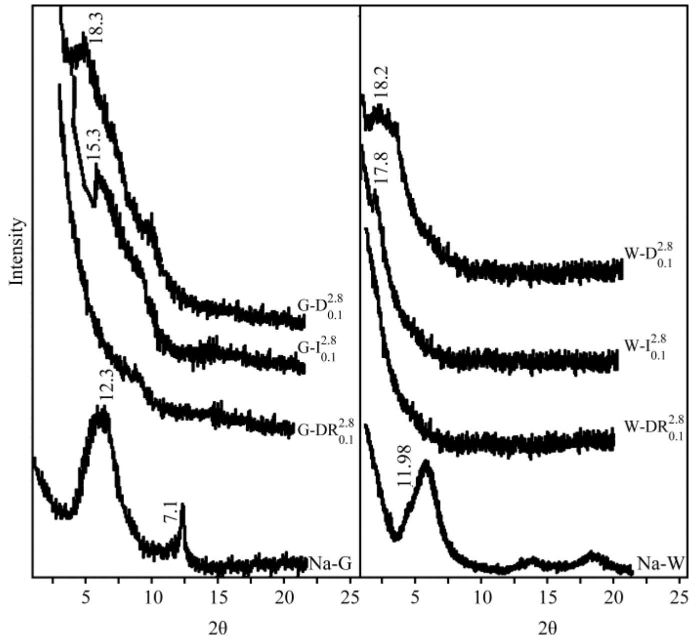


Fig. 7. X-ray diffractograms of Na-bentonite and Zr-pillared samples with different methods.

Table 5. Textural properties of starting and Zr-pillared clays

	S_{BET} (m^2/g)	$S_{externe}$ (m^2/g)	S_{micro} (m^2/g)	V_p (cm^3/g)	$V_{\mu p}$ (cm^3/g)	CEC (meq/100g)	ZrO_2(%)	$^*ZrO_2$(%)	Al_2O_3(%)
Na-G	107.2	67.5	39.7	0.15	0.02	78	0	0	24.80
$G-D_{0.1}^{2.8}$	199.5	77.3	122.2	0.21	0.06	24	16.71	16.54	20.34
$G-DR_{0.1}^{2.8}$	190.6	65.7	124.9	0.18	0.06	47	28.45	16.20	16.56
$G-I_{0.1}^{2.8}$	187.1	68.7	118.4	0.19	0.06	23	13.42	13.36	21.26
Na-W	112	59.67	52.53	0.15	0.02	98	0	0	23.34
$W-D_{0.1}^{2.8}$	192.5	87.6	104.9	0.21	0.05	26	17.35	17.31	21.30
$W-DR_{0.1}^{2.8}$	189.9	75.8	114.1	0.19	0.05	44	29.44	15.31	18.43
$W-I_{0.1}^{2.8}$	174.6	90.3	84.3	0.17	0.048	29	15.25	15	21.99

*: *after exchange with* NaCl (1M)

Table 6. PZC values obtained by mass titration and potentiometric titration for different samples

Samples	PZC (mass titration)	PZC (potentiometric titration)	Acid center(mmol/g)
Na-G	7.27	7.33	0.76
$G-D_{0.1}^{2.8}$	4.7	4.72	1.21
$G-I_{0.1}^{2.8}$	4.74	4.75	0.92
$G-DR_{0.1}^{2.8}$	4.82	4.85	0.78
Na -W	8.60	8.57	0.86
$W-D_{0.1}^{2.8}$	4.69	4.75	1.43
$W-I_{0.1}^{2.8}$	4.81	4.78	1.11
$W-DR_{0.1}^{2.8}$	4.73	4.88	0.94

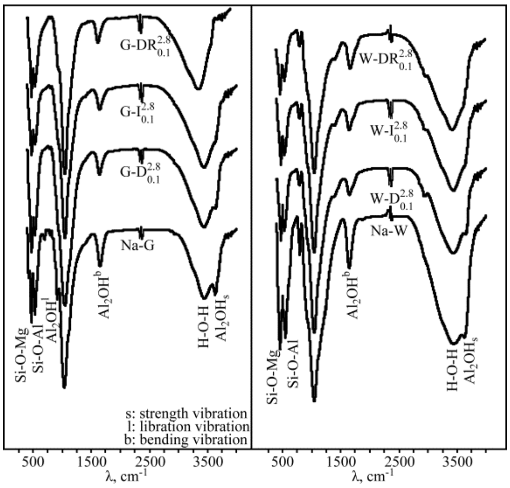


Fig. 8. FT-IR spectra of the two Na-clays before and after Zr-pillaring.

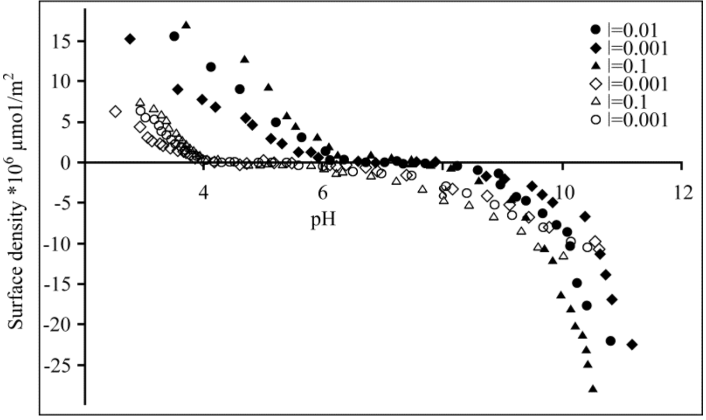


Fig. 9. Potentiometric titration curves for $\mathrm{G-D}^{2.8}_{0.1}$ (filled symbols), and Na-G (open symbols).

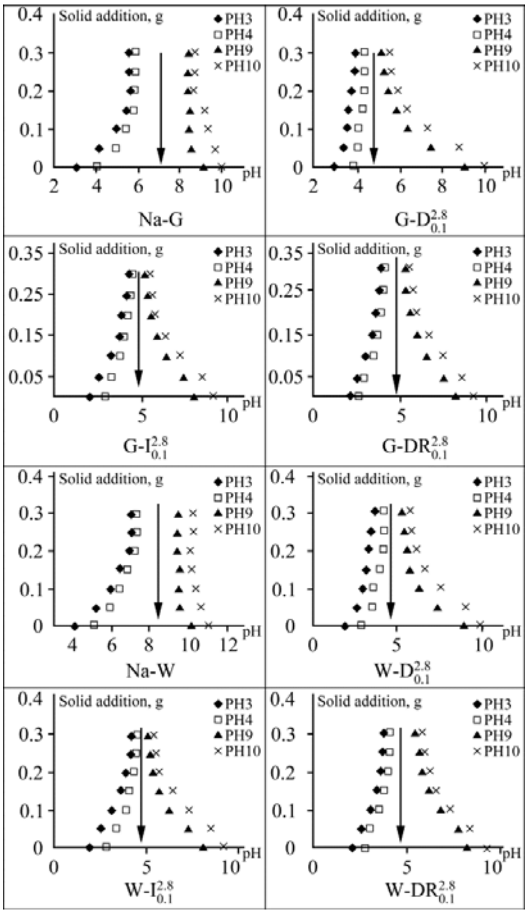


Fig. 10. Mass titration curves of Na-bentonite and Zr-PILCs.

Results reported in Table 6 indicate that the acidity of the clay is enhanced by pillaring. As can be seen from this Table, all of the PILCs contained enormously high surface acidity compared to the Na-bentonite. Among the three method, the number of acid centers increases in the following order: ‘DR’ Method < ‘I’ Method < ‘D’ Method. The number of acid centers does not correlate with the surface area of the solids.

In addition, an IR study has been performed by the adsorption of Butylamine on the clay surface to further identify the surface acidity of the clay. The spectra from 1400 to 1800 cm^{-1} given in Fig. 11 show five major adsorption bands at 1445, 1490, 1540, 1590 and 1623 cm^{-1}. The bands at 1445, 1590 and 1623 cm^{-1} are mainly assigned to the Lewis acid site. The band at 1490 cm^{-1} is attributed to both Lewis and Brönsted acid sites. The peak at 1540 is assigned to the Brönsted acid site. The results of the surface acidity indicate that the Zr-PILCs exhibited better Brönsted and Lewis acidity as compared to the starting form of the Na-bentonite.

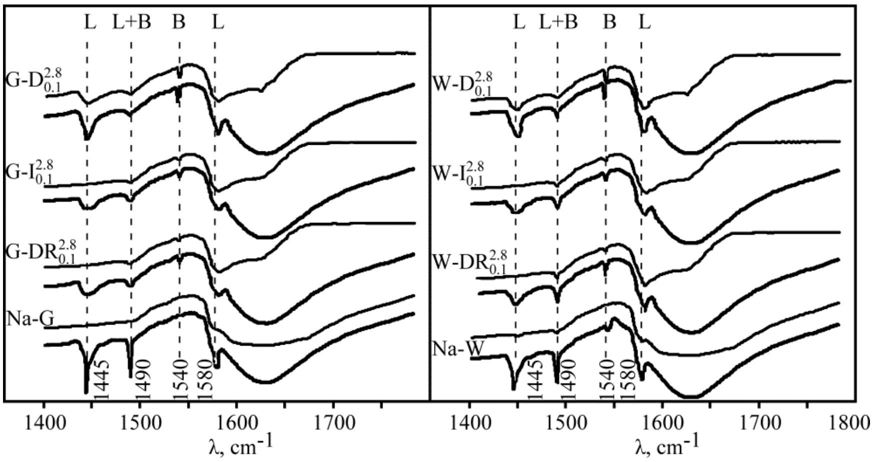


Fig. 11. FT-IR spectra of Butylamine adsorbed on Na-Clay and Zr-PILCs (▬ at 298K and – treated at 673 K).

Table 7. Yield of 2,2-diméthyl-1,3-dioxolane catalyzed by original and modified clays

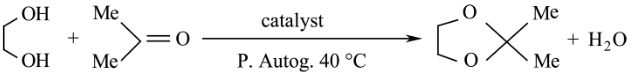
Sample	*	Na-bentonite	G – D$^{2.8}_{0.1}$	G – I$^{2.8}_{0.1}$	G – DR$^{2.8}_{0.1}$	W – D$^{2.8}_{0.1}$	W – I$^{2.8}_{0.1}$	W – DR$^{2.8}_{0.1}$
Yield (%)	0	0	41	25	17	42	26	9

**: reaction without catalyst*

Next, it was proved that the nature of an acid center depends on the pillaring method. In fact, PILCs prepared with the ‘D’ method contain stronger Brönsted and Lewis acid sites that remain after treatment at 400°C. However, on the thermal treatment at 400°C, the band at 1445 cm^{-1} in the spectrum of samples prepared by the ‘DR’ and ‘I’ methods disappeared, indicate that at this temperature the Lewis sites available are not strong enough to interact with n-butylamine. The intensities of the bands assigned to Butylamine coordinated onto the Lewis and Brönsted acid sites are stronger in the case of solids obtained by the direct (D) method.

Catalytic activity for dioxolane forming

Solids prepared with the three methods were used as catalysts in the reaction of acetalization of acetone with ethylene glycol (Scheme). The use of Zr-PILLCs as catalysts for this type of reaction is reported for the first time.



Scheme

It should be noted that this reaction was also performed using the starting clays and without any catalyst. The yield of the product results was obtained from ^{1}HNMR spectrum data. The analysis of the results in Table 7 shows that no product was formed in the absence of a catalyst and in the presence of the two starting clays. However, all Zr-PILLCs are active for this reaction but with a different yield of the corresponding ketal. The variation in the yield depends mostly on the pillaring method. In fact, the direct method gives samples having the highest activity, while samples obtained by the ‘DR’ ones showed the lowest. The solid obtained with the inverted method exhibited activity, which was intermediate between the two.

This variation of activity among the three methods cannot be explained on the basis of their surface area but on the number and type of the acid center. Herein, the reason for the higher activity of solid prepared by the direct method is its higher number of acid sites and the strength of Lewis acid center as compared to samples obtained with ‘DR’ and ‘I’ method keeping in mind that this reaction needs an acid catalyst.

CONCLUSION

In this paper, an investigation of Zr-PILCs prepared from the two bentonites has been performed. We have found out that the Tunisian clay (G) presented a behavior that is similar to the commercial Wyoming clay (W). The study of the preparation parameters of Zr-PILLCs using zirconium tetrachloride as precursor shows that:

1. The dialysis stage is a determining factor in the polymerization of zirconium, and the arrangement of the intercalated structure in the interlamellar space stops during washing.
2. The pH of the starting Zr solution is, in particular, of primary importance in getting the proper Zr species and pillared materials.
3. Under reflux conditions a delamination of the clay structure and its partial dissolution were observed.
4. The method employed in the Zr-PIILCs synthesis affects essentially the surface acidity.
5. The optimum conditions of the pillaring process using the tetrachloride precursor are: pH = 2.8, $[Zr^{4+}]_i$ = 0.1M, five dialysis and the direct method 'D'.
6. The study of a catalytic activity indicates that the acidity number and the type of the catalyst play an important role in the reaction of acetalization.

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Реферат

Целью работы является изучение твердых веществ, полученных путем интеркаляции тунисского бентонита циркониевыми поликатионами, с помощью гидролиза тетрахлорида циркония. Для сравнения в качестве контрольной глины изучается также интеркалированный монтмориллонит из штата Вайоминг. Варьирование таких процессов синтеза, как количество диализов, концентрации раствора Zr, pH, температуры и метода выемки, оказывало влияние на структуру и свойства полученной глины. Было установлено, что структура интеркалированной глины сильно зависит от метода её приготовления и pH: в одних случаях были получены упорядоченные интеркалированные глины (с базальными промежутками от 15 до 18,2 A), тогда как в других случаях были получены нанокристаллические твердые вещества. Деламинация глин наблюдается в обоих случаях, когда интеркаляция растворов, полученных из тетрахлорида циркония имеет pH > 2,8 или когда они подвержены воздействию рефлюкса. Наилучшие результаты были получены при использовании пяти диализов при pH = 2,8 $[Zr^{4+}]$ = 0,1 M, при комнатной температуре и прямом методе. Удельная общая площадь поверхности и объем микропор твердых веществ достигали 200 $м^2$ g^{-1} и 0,06 $см^3$ g^{-1}, соответственно. Данные потенциометрии и масс-титрации показывают, что в интеркалированном материале происходит сдвиг заряда с нулевой точки к нулевой точке заряда оксида циркония. Установленное количество ZrO_2 менялось от 6 до 30% от веса интеркалированных образцов. Была исследована активность глины с использованием циркония для синтеза 1,3-диоксолана. Метод интеркаляции оказывает решающее влияние на эту реакцию.

Ключевые слова: Zr-олигомер, интеркалированная глина, PZC, 1,3-диоксолан, ацетализация.