

Effect of Temperature Synthesis on the Catalytic Performance of Zirconium Pillared Interlayered Clays for Phenol Oxidation

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Abstract

Zirconium pillaring solutions have been prepared at different temperatures in order to investigate their effect on the physico-chemical properties of the resulting pillared clays. It has been verified that variation in the temperature affects the properties of the pillared clays obtained. The resulting materials exhibited basal spacings in the range of 18-19.5 Å, except for pillared interlayered clays (PILCs) prepared at a temperature $\geq 75^\circ\text{C}$, whose structure collapsed below 550°C . Improvements in specific surface area ($200\text{-}250\text{ m}^2\text{g}^{-1}$) were achieved. Fixed zirconium ranges between 15.3 and 17%. Stronger Bronsted acid sites were developed into the Zr-PILCs materials, in addition to Lewis sites, even at 500°C , as indicated by the desorption of n-butylamine as a probe molecule. These acid sites were strong enough to convert phenol to CO_2 and H_2O .

Keywords: Zr-pillared clays; Heterogeneous catalysis; Catalytic oxidation; Phenol; Hydrogen peroxide

Introduction

It is clear today that sustainable development in any society requires chemical processes to be cleaner and cleaner, which involves avoiding the formation of harmful residual subproducts [1]. This is not always possible. Thus, it is necessary to turn to the implementation of proper technologies for the elimination of such residues. Organic compounds are among the main pollutants found in waste waters, such as phenol, substituted phenols (chlorophenol, nitrophenol), pesticides, and herbicides, among others [2-4]. Phenol in particular is considered to be one of the most toxic pollutants [3,5]. Catalytic wet air oxidation (CWAO) is an efficient technique to eliminate organic compounds such as phenols [6]. Homogenous and heterogeneous catalysts were developed using strong oxidants such as H_2O_2 [7-13]. Homogeneous catalysts (Cu^{2+} and Fe^{2+}) must be separated from the aqueous solution after the reaction, which in turn increases the costs of the process and brings about further contamination through the dissolved metal ions. The use of heterogeneous catalysts constitutes a true alternative for the phenol oxidation in aqueous medium if the catalyst is stable in an aqueous medium and selective towards the formation of CO_2 and H_2O [14]. Pillared clays represent a new class of microporous materials that have potential catalytic application in phenolic molecule degradation [15]. Pillared clays prepared by the intercalation of inorganic cationic clusters into clay layers and subsequent thermal activation, have been extensively investigated as catalysts and catalyst supports. Pillared clays provide many advantages over the parent clays. The uniform pore structure of pillared clay combined with its acidity and thermal stability has been crucial for many organic and shape selective reactions. By using suitable chemical methods, polycations obtained from the polymerization of multivalent inorganic cations have been intercalated into the interlayer region of clays. Among all the pillared

clays, clays pillared with inorganic polycations of Al and Zr have been most widely investigated due to their relatively simple way of preparation and variety of catalytic applications. In the case of Zr-PILCs, it was reported that the polycationic pillaring species is $(\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16})^{8+}$ [16-20]. The final property of the Zr-pillared clays depends upon several factors such as the method of intercalation. The intercalation of clays with zirconium oligomers has been widely studied. Nevertheless, few preparation methods for zirconium intercalated. Two main methods of preparation of Zr pillared interlayered clays have been reported in the literature, described a method in which a clay suspension is mixed with a fresh ZrOCl_2 solution to produce, upon hydrolysis at room temperature, a zirconium oligomer whose structure is the square planar complex $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}\text{Cl}_2]^{(8-z)+}$ [21]. Bartley and Burch; Ohtsuka et al. considered the reflux at 100°C of ZrOCl_2 solutions before and after addition to the clay suspension, to favour the polymerization of the zirconium complex [22,23]. The main drawback of these methods is the longer preparation time. Therefore, effort were made to reduce the intercalation period by using a novel route, which comprise the use of ultrasonication and microwave techniques for preparation of Zr-pillared clays [24-26]. In the synthesis of zirconia pillared clays, one of the principal pillared clays quoted in the literature, zirconium oxychloride solutions are commonly used as the pillaring precursors [27,28]. Zirconium acetate was also used as Zr precursor, in order to minimize dealumination of the clay structure but, few papers describing the pillaring with zirconium oligomers using ZrCl_4 as a source of zirconium species has been published [19,29-31] to the best of the authors' knowledge. Genesis of the metal oxyhydroxide polycations, washing and drying steps are also key factors in controlling the nature of the zirconium species present in solution, which are responsible for the intercalation process [32-37]. 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, to study the effects of the temperature of the pillaring solution on the structural and

textural properties of Zr pillared Tunisian bentonite. Then, the application of the pillared bentonite as a catalyst in the phenol oxidation reaction is also investigated.

Experimental Conditions

The dye concentrations were measured using ELICO SL 27 VIS Spectrophotometer. Brilliant Green (BG) is used in the adsorptive technique was obtained from HI media laboratory pvt ltd, Mumbai. The coconut shells were received from domestic waste.

Preparation of Na-bent

In order to prepare the pillared materials, the bentonite was purified by conventional sedimentation. To eliminate the calcite (23%, measured by calcimetry), crude bentonite was first treated with 0.3 M HCl. The pretreated sample was then stirred for 12 h at room temperature and at a rate of 100 g l⁻¹ in a molar solution of sodium chloride. The suspension was then centrifuged at 3000 rev min⁻¹. The ion exchange was repeated five times. After the final centrifugation, the clay exchanged with sodium was washed by centrifugation and then separated from its impurities by sedimentation/decantation. Finally, removal of the excess chloride by dialysis with distilled water gave Na-bentonite (Na-Bent). The chemical composition of the Na exchanged purified fraction, expressed in the oxide form/100 g of the calcined sample, is SiO₂ 61.38, Al₂O₃ 24.80, Fe₂O₃ 8.03, Na₂O 3.06, MgO 1.38, CaO 0.13, K₂O 1.40. The structural formula of Na-Bent was found to be: ^{IV}[Si_{7.43}Al_{0.57}]^{VI}[Al_{2.96}Fe_{0.73}Mg_{0.24}]Na_{0.71}K_{0.21}Ca_{0.01}O₂₂. Its cation exchange capacity (CEC) is 78 meq/100 g and its specific surface area is: SBET=107 m² g⁻¹.

Synthesis of the pillared clays

A zirconium polycation solution was prepared at different temperature (25°C, 40°C, 50°C, 75°C, and, 100°C) by slow titration of a ZrCl₄ solution (0.1 M) with a solution of NaOH (0.2 M) under vigorous stirring, using a OH/Zr mole ratio equal to 4 (pH=2.8). This value of pH allows to a thermally stable zirconium pillared clays with controlled morphology, texture and acid properties (saida and frini surface engineering). The pillaring solutions were then aged for 24 hours at 25, 40, 50, 75, and 100°C. The pillared interlayered clays were obtained by addition of various aqueous solutions of hydroxy-zirconium to 5 g of the Na-Bent clays, using a ratio Zr/clay of 10 mmol/g. This ratio is the most widely used in the literature either for Zr-PILCs or Al-PILCs [18,29,38-47]. The suspensions were kept in contact with the solution for 24 hours at 25, 40, 50, 75, and 100°C), washed by centrifugation and dialysis (five times) and dried at 60°C, then calcined at 550°C for 2 h according to the literature [30,48,49]. The samples are designated by the following nomenclature: Zrx-Bent, where the subindex indicates the temperature of pillaring solution.

Physico-chemical characterization

The X-ray diffraction (XRD) study was done in a 'PANalytical X'Pert HighScore Plus' device, which operates with Cu K α radiation.

N₂ adsorption-desorption experiments were carried out at -196°C on a Quantachrome, USA instrument. The N₂ isotherms were used to determine the specific surface areas (SBET) using the BET equation. The micropore volume was determined using the t-plot method and the total pore volume of the samples, V_t, was calculated at P/P₀=0.99. Before each measurement the samples were outgassed for 2 h at 130°C.

The chemical analysis of the starting material and modified samples was determined by atomic adsorption, the spectrometer used is of the type AAS Vario.

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

Potentiometric titration measurements were performed with a Titrand 716 automatic titrator (Metrohm) at ambient temperature and aerated medium. The PZC value and acid centre were determined following the method described by Sposito [50]. Using the proton adsorption or proton charge σH (mol m⁻²) the following formula was applied,

$$\sigma H(\text{mol m}^{-2}) = \frac{v}{m} S \left\{ \left(\left[H^+ \right]_b - \left[H^+ \right]_a - K_w \left(\frac{1}{\left[H^+ \right]_b} - \frac{1}{\left[H^+ \right]_s} \right) \right\}$$

Where V is the volume of electrolyte solution equilibrated with clay (50 ml), [H⁺] is the solution proton concentration (M), K_w is the dissociation product of water (10⁻¹⁴), subscripts 's' and 'b' refer to sample and blank solution, m is the mass of sample used (0.05 g), and S is the specific surface area (m²g⁻¹).

The PZC values were also determined following the method described by, mass titration experiments were performed followed by the pH drift until a steady value was achieved [51]. 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 minutes. Then a new amount of the sample was introduced to make changes in the pH. This procedure was repeated until no pH change occurred.

Brönsted and Lewis acid centers were determined by FT-IR spectroscopy method on the basis of adsorption of butylamine. With this method 10 ml of prepared butylamine in a cyclohexane solution was added to 0.1 g of catalyst. The mixture was shaken at room temperature. After drying at room temperature for 48 h, each sample was outgassed at different temperatures. FT-IR spectra were recorded in the region 1800–400 cm⁻¹ on a Perkin-Elmer infrared Fourier transform spectrometer using the KBr pellet technique.

Catalytic study

The catalytic oxidation reaction of phenol in a diluted aqueous medium was carried out in a batch reactor (pyrex) with a capacity of 250 mL, open to the atmosphere, thermostatted at 25°C, thoroughly stirring and constantly monitoring the pH variations by means of an electrode. The device featured an automatic dosimeter (Dosimat 725 Metrohm) for the continuous addition of the oxidizing agent (hydrogen peroxide solution). For each test the reactor was loaded with 100 mL of a phenol solution (5 × 10⁻⁴ M) and 0.5 g of catalyst. The hydrogen peroxide solution (0.5 M) was added at a 2 mL h⁻¹ flow. The pH was continuously adjusted to 3.7 with dilute aqueous HCl or NaOH solutions (0.1 M) and an air flow was introduced in the reactor at a ratio of 2 L h⁻¹. The course of the phenol conversion and the appearance of the intermediate compounds were followed by high-performance liquid chromatography (HPLC) by means of a Waters 600 E liquid chromatographer equipped with an aminex HPX 87 H

(Biorad) column. The evaluation of the total organic carbon (TOC) was carried out with a Dohrman DC-80 device.

Results

Characterization of samples

XRD: The oriented powder XRD traces of the pillared clays calcined at 550°C are shown in Figure 1. The results indicate that the modification carried out on the clay leads, when the pillaring solutions were prepared at a temperature under 75°C, to the successful pillaring of the material. In fact, the shift of the d001 basal spacing from 10 Å (starting clay) to 18.22-19.5 Å (Table 1) confirms the modification via pillaring. And, indicating that the layers of the clay are homogeneously spaced. However, in the case of samples prepared with a high temperature (75°C and 100°C), it must be emphasised that the clay structure becomes disordered, thus giving products on which the (001) reflection peaks disappear. Basal spacings of the samples, at 25°C and calcined at 550°C, are presented in Table 1.

The preparation of the pillared clays at a temperature $\leq 50^\circ\text{C}$ was favourable for the production of a homogenous product as shown in

Table 1. This positive effect could be explained by a better homogeneous expansion of the clay layers, which favours the diffusion of ions in the interlamellar space. At higher temperature (75°C and 100°C), a product with a non-crystalline structure was obtained (Figure 1). The broadness of the 001 diffraction peak is widely reported in the literature [38,52]. This indicates a poorly ordered structure showing the presence of different polymer species (irregular intercalation) and possible delamination of the clay structure. Fetter et al. Reported that the expected zirconium species present, among others, in solution is the hydroxylation $[\text{Zr}_4\text{OH}_8(\text{H}_2\text{O})_{16}]^{8+}$, which rapidly polymerizes to form other species [26]. Then the montmorillonites are expected to be intercalated with different sizes causing the irregular staking of the clay layers. Farfan-Torres et al. reported that samples prepared at 100°C is an amorphous solid [16]. And he observed that there is an increase in the ZrO_2 loading for higher temperature, but with alteration of the clay structure, same behavior obtained by us.

To avoid further degradation of the clay, as shown in Table 1, the temperature must be between 25°C and 50°C to favor the polymerization of zirconium complex.

| | $d_{001}(\text{Å})$ | |
|-------------------------|---------------------|-------------|
| | 25°C | 550°C |
| Na-Bent | 12 | 10 |
| Zr ₂₅ -Bent | 19.7 | 18.2 |
| Zr ₄₀ -Bent | 21.2 | 19.4 |
| Zr ₅₀ -Bent | 21 | 19.5 |
| Zr ₇₅ -Bent | delaminated | delaminated |
| Zr ₁₀₀ -Bent | delaminated | delaminated |

Table 1: Basal spacing of Zr-Bent at 25°C and at 550°C.

Chemical analysis: The evolution of the ZrO_2 introduced by pillaring process between layers as function of the different temperature is shown in Table 2. The ZrO_2 percentage of the Zr-Bent prepared at a temperature between 25°C and 50°C are almost the same. In fact, the ZrO_2 percentages are 16.7%, 17.1% and 17.3% for Zr₂₅-Bent, Zr₄₀-Bent and Zr₅₀-Bent samples respectively. Concerning the samples prepared at higher temperature, there is an increase in ZrO_2 loading. The maximum percentage of ZrO_2 introduced is reached with Zr₇₅-Bent and Zr₁₀₀-Bent samples (28 and 31% respectively). Two hypotheses may be proposed to explain the increase in the amount of zirconium: (i) the excess of pillaring agent may be adsorbed on the interlayer and external surfaces as neutral species ($\text{Zr}_4(\text{OH})_{16}$) or $\text{Zr}(\text{OH})_4$ (ii) a modification of the zirconium pillars by hydrolysis and/or polymerization due to the augmentation of temperature was produced [16,21]. Given broadness of the 001-diffraction peak obtained in the case of the Zr₇₅-Bent and Zr₁₀₀-Bent samples, it seems likely that the large amount of polycations introduced may be related

to the formation of the neutral species rather than the form or arrangement of the pillars. The fixed zirconium exchanged is the quantity of Zr that remains linked to the structure after calcination and, in consequence, is not exchangeable with another cation if PILCs are redispersed in water. The quantity of the fixed zirconium exchanged was measured by a method similar to that used by Yamanaka and Brindley using CaCl_2 solution [21]. In this way, the pillared samples, are redispersed in NaCl (1 M) solution. Results show that the Zr fixed is not exchangeable with Na^+ cation when PILCs are redispersed in NaCl (1 M) solution except for samples prepared with a temperature equal 75°C or 100°C (Table 2). The chemical analysis data of Zr₇₅-Bent and Zr₁₀₀-Bent solids, after dispersing in the NaCl solution (1 M), showed that about half of zirconium was detected in the solution of NaCl. This amount was removed by exchanged reaction (Table 2). So, the large amount of polycations introduced may be related to the formation of the neutral species rather than the form or arrangement of the pillars.

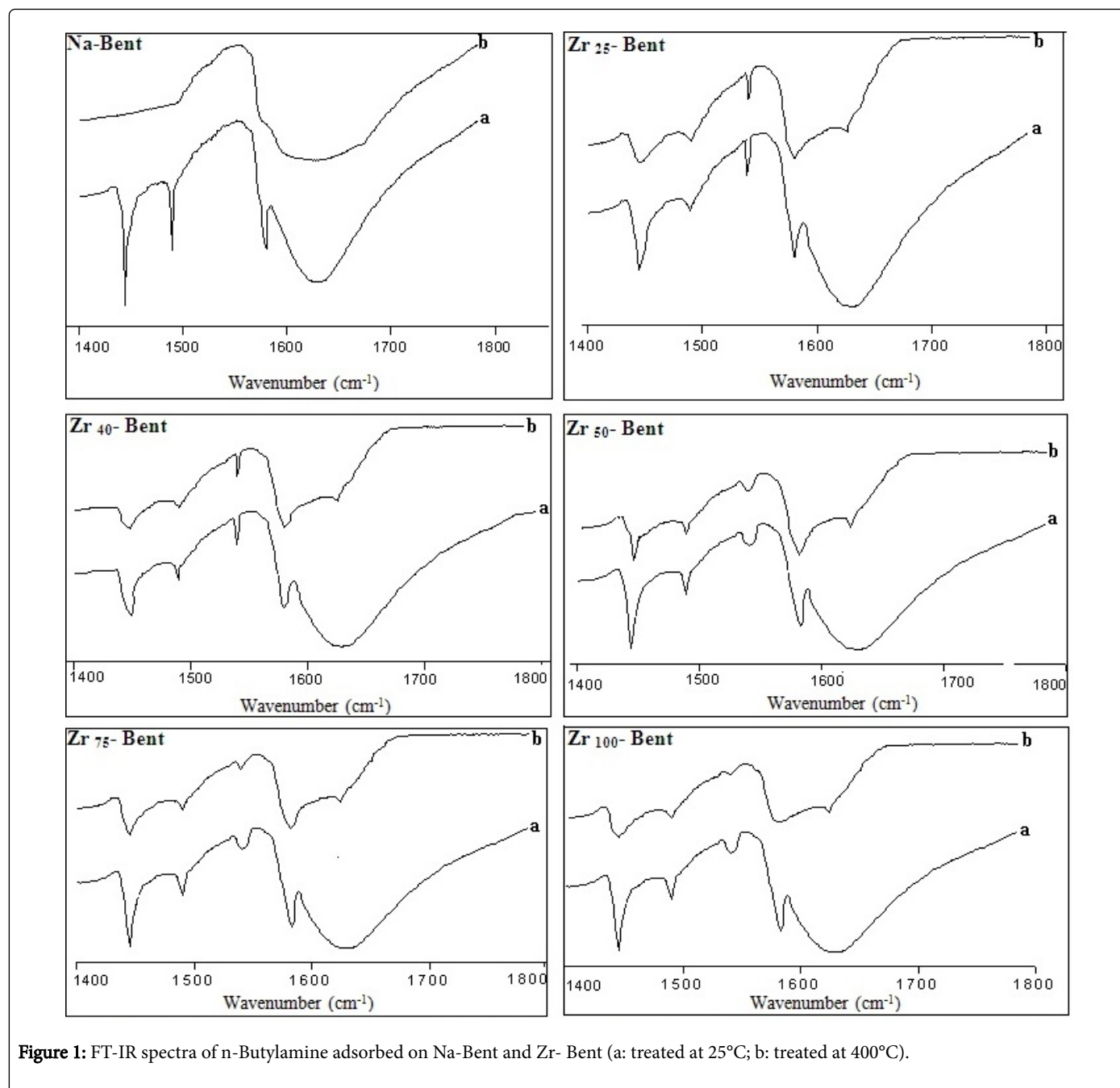


Figure 1: FT-IR spectra of n-Butylamine adsorbed on Na-Bent and Zr- Bent (a: treated at 25°C; b: treated at 400°C).

CEC: The residual cation exchange capacity (CEC) of calcined samples are presented in Table 3. It has to be noted that residual CEC are rather small in comparison with initial CEC of Na-Bent (78 meq/100 g of clay). It is clear from the Table 3 that the residual CEC decreases as a function of the total ZrO₂ fixed between layers (Table 2). The high residual CEC for Zr₇₅-Bent and Zr₁₀₀-Bent samples (41 and 44 meq/100 g) and the decrease of the zirconium amount after its

redispersion in the 1 M NaCl solution (Table 2) prove the existence of a part of zirconium that is not irreversibly fixed to the structure. This behaviour could be explained as a certain amount of Zr that may be adsorbed as a neutral species such as Zr₄(OH)₁₆ [21]. The existence of those neutral species in the interlamellar space explains the amorphous structure detected.

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MgO | CaO | K ₂ O | Na ₂ O | ZrO ₂ | ZrO ₂ ' (Wt,%) |
|---------|------------------|--------------------------------|--------------------------------|------|------|------------------|-------------------|------------------|---------------------------|
| Na-Bent | 61.38 | 24.8 | 8.03 | 1.38 | 0.13 | 1.4 | 3.06 | 0 | 0 |

| | | | | | | | | | |
|-------------------------|-------|-------|------|------|------|------|------|-------|------|
| Zr ₂₅ -Bent | 52.09 | 20.34 | 7.59 | 1.37 | 0.12 | 1.19 | 0.64 | 16.71 | 16.5 |
| Zr ₄₀ -Bent | 52.08 | 20.37 | 7.58 | 1.36 | 0.09 | 1.16 | 0.24 | 17.1 | 17 |
| Zr ₅₀ -Bent | 52.07 | 20.36 | 7.55 | 1.31 | 0.11 | 1.15 | 0.34 | 17.3 | 17 |
| Zr ₇₅ -Bent | 44.5 | 18.31 | 6.54 | 1.3 | 0.11 | 1.11 | 0.14 | 28 | 15.7 |
| Zr ₁₀₀ -Bent | 43 | 16.98 | 6.59 | 1.22 | 0.09 | 1.12 | 0.13 | 31 | 15.3 |

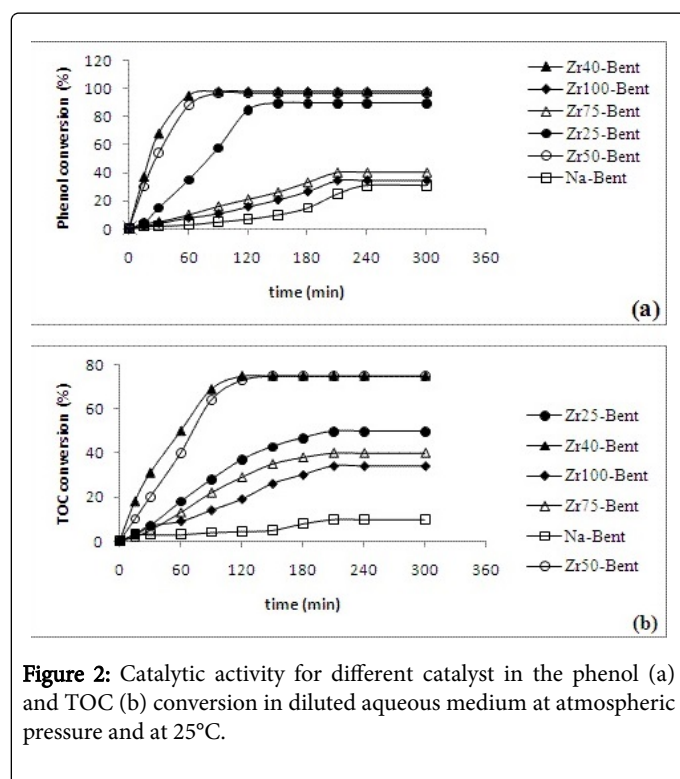
Table 2: Chemical composition of Na-Bent-G and other pillared samples.

* After exchange with NaCl (1 M).

| Samples | SBET (m ² g ⁻¹) | S _{up} (m ² g ⁻¹) | V _p (cm ³ g ⁻¹) | V _{up} (cm ³ g ⁻¹) | CEC (meq/100 g) |
|-------------------------|--|---|---|--|-----------------|
| Na-Bent | 107 | 40 | 0,15 | 0 ,021 | 78 |
| Zr ₂₅ -Bent | 200 | 132 | 0,21 | 0,063 | 24 |
| Zr ₄₀ -Bent | 250 | 183 | 0,21 | 0,067 | 22 |
| Zr ₅₀ -Bent | 247 | 185 | 0,21 | 0,069 | 22 |
| Zr ₇₅ -Bent | 180 | 81 | 0,16 | 0,045 | 41 |
| Zr ₁₀₀ -Bent | 190.6 | 90 | 0.16 | 0.033 | 47 |

Table 3: Textural properties and CEC of starting material and Zr-PILCs.

Specific surface area and porosity: Figure 2 shows the adsorption desorption isotherms of some samples. The adsorption isotherms are of type I in the Brunauer, Deming, Deming and Teller (BDDT) classification at low pressures. All samples show a hysteresis loop type H3 in the IUPAC classification. The specific surface area (SBET) and microporosity of starting and modified clays are included in Table 3. For the initial bentonite, almost all the surface area results from pores in the mesopore size range. In contrast, for the pillared clays, an important portion of the specific surface area depends on micropores [53,54]. As expected, the presence of zirconium pillars produces important modifications in the specific surface area values. Almost, the intercalation with zirconium polycation caused a noticeable increase of the specific surface areas. The increase of surface area for the pillared samples is essentially related to the creation of micropores by the pillaring process and confirms that the pillar species used during preparation had entered between the clay layers, increasing the nitrogen accessibility. The resulting surface areas of Zr₄₀-Bent and Zr₅₀-Bent were larger than that prepared under conventional preparation (Zr₂₅-Bent). So, the preparation of zirconium pillars at 40 or 50°C was favorable for the production of microporous product. However, heating the zirconium solution at higher temperature (75 and 100°C) produces a low specific surface area. This behavior can imply that these samples have lower accessibility to the N₂, which is due to the smaller size of the pores caused by blocking of the interlayer spacing. This correlates well with the result given by XRD data which indicates the presence of amorphous products obtained with 75°C and 100°C. Under this preparation condition, dissolution of clay with the formation of colloidal silica could take place, as reported in early studies concerning acid activation of clay [55].



Acidity: The origin of the electrical charge of bentonite is of two kinds: a permanent charge σO created by isomorphic substitution of Al^{3+} for Si^{4+} in mineral structure and a variable charge σH (pH depending) on the edge resulting from proton adsorption/desorption reaction on surface hydroxyl groups. Depending on pH, these surfaces

can bear net negative, or positive, or no charge. The pH where the net total particle charge is zero is called the point of zero charge (PZC), which is one of the most important parameters used to describe variable charge surfaces. An example of the curve σ Hvs. pH for Na-Bent and Zr₂₅-Bent samples at three different ionic strengths is shown in Figure 3. The point of zero charge (PZC) and the number of acid centres in Na-Bent-G and modified clay, determined following the method of Sposito, are reported in Table 4 [50]. The PZC values of pillared samples are lower than the PZC of starting clay, the acidity of the clay is enhanced by pillaring. The intercalation of Zr species produced a shift of PZC from 7.3 for Na-Bent clay to [4.2-5.3] for the Zr-Bent pillared sample. This value is in good agreement with the PZC value of ZrO₂ reported in the literature, which ranges from 4 to 5 [56]. The PZC values depend directly on the amount of zirconium introduced into the clay. This shows that the acidity increases with the amount of the fixed zirconium exchanged. Zr₄₀-Bent and Zr₅₀-Bent samples have lower PZC and therefore show higher surface acidity. Preparation of Zr-solution at a temperature up to 50°C reduces the acidity of the resulting catalyst.

Based on the total acid site numbers, the Zr₅₀ sample has the highest total acidity (1.75 mmol/g). We notice that this sample is the richest in zirconium. The acidity found by us for zirconium pillared clay using ZrCl₄ is higher than that reported by Toranzo et al. which reaches 0.66 and 0.87 mmol H⁺/g (of bentonite) when using zirconium acetate and zirconyl (ZrOCl₂) respectively as precursors [57].

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 [51]. As is shown in Figure 3, 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 pH are reported in Table 4 and marked with arrows in Figure 3. It is possible to deduce here that there is very good agreement between acid-base potentiometric titrations and mass titration.

The infrared spectra of N-butylamine adsorbed on the original clay and Zr-Bent after evacuation at different temperatures. According to Awate et al., the bands at 1450 and 1590 cm⁻¹ are commonly assigned to Lewis acidity, the one at 1490 cm⁻¹ is mainly attributed to both Lewis and Brønsted acidity, and the peak at 1545 cm⁻¹ and the shoulder of the IR band at 1639 cm⁻¹ are due to Brønsted acidity [27]. Ruiz et al. also reported that n-butylamine thermodesorption give results similar to pyridine thermodesorption [58].

The results of surface acidity measurements indicated that the modified forms of clay exhibited better Bronsted and Lewis acidity when compared to their starting form, the Na-Bent sample, which presents only weak Lewis acid sites at 298 K. The acidity of Zr-PILCs

may arise from the hydroxyl groups attached to Zr and the structural hydroxyl groups in the PILC [59-61]. During calcination, ion exchanged Zr poly-hydroxy-cation is converted into hydrated ZrO₂ pillars and structural hydroxyl groups attached to Al/Mg are formed [35]. On thermal treatment at 673 K, a slight reduction in the intensity of the peaks of both Bronsted and Lewis acidity was observed in the case of all samples. This indicates stronger acidity of those samples. Farfan-Torres et al. reported in earlier study that the presence of amorphous phases suggests the formation of Bronsted acid sites on the solids calcined at 673 K [16].

The Bronsted/Lewis (B/L) ratio were obtained by integration of the area of the adsorption bands shown in Figure 3. The peak areas were used to measure the intensity of the bands. According to Grim, only bands at 1545 cm⁻¹ (Bronsted acidity) and at 1448 cm⁻¹ (Lewis acidity) have to be taken into account to evaluate the two types of acidity. The B/L ratios at 298 and 673 K are reported in Table 5. As it can be seen, the B/L ratio decreases for all samples after thermal treatment. For the B/L ratio at 673 K, it is notably high in the case of Zr₄₀-Bent and Zr₅₀-Bent.

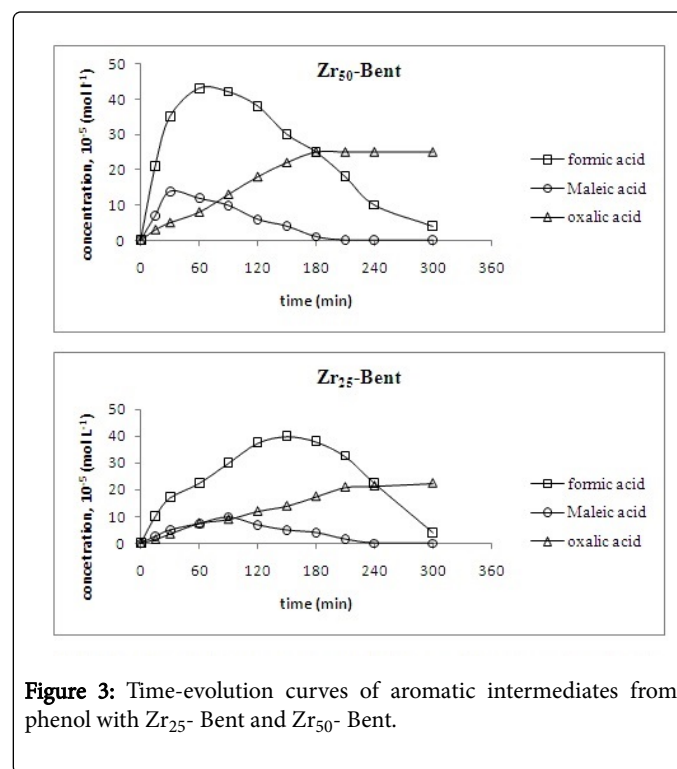


Figure 3: Time-evolution curves of aromatic intermediates from phenol with Zr₂₅-Bent and Zr₅₀-Bent.

| | PZC (mass titration) | PZC (potentiometric titration) | Acid center (mmol/g) |
|------------------------|----------------------|--------------------------------|----------------------|
| Na-Bent | 7.31 | 7.33 | 0.76 |
| Zr ₂₅ -Bent | 4.73 | 4.71 | 1.21 |
| Zr ₄₀ -Bent | 4.22 | 4.25 | 1.65 |
| Zr ₅₀ -Bent | 4.23 | 4.26 | 1.75 |
| Zr ₇₅ -Bent | 4.91 | 4.98 | 0.93 |

| | | | |
|-------------------------|------|------|------|
| Zr ₁₀₀ -Bent | 5.31 | 5.33 | 0.88 |
|-------------------------|------|------|------|

Table 4: B/L ratio values of Na-Bent and Zr-Bent obtained at 25°C and 400°C.

| | Na-Bent | Zr ₂₅ -Bent | Zr ₄₀ -Bent | Zr ₅₀ -Bent | Zr ₇₅ -Bent | Zr ₁₀₀ -Bent |
|------------|---------|------------------------|------------------------|------------------------|------------------------|-------------------------|
| B/L(25°C) | 0 | 0.29 | 0.33 | 0.4 | 0.21 | 0.23 |
| B/L(400°C) | 0 | 0.25 | 0.3 | 0.38 | 0.18 | 0.19 |

Table 5: PZC values obtained by mass titration.

Catalytic activities

An important characteristic is the improved catalytic sites that influence the catalysis rate.

Figure 2 shows the results obtained for phenol conversion and total organic carbon TOC reduction with the different catalyst. It is clearly seen that the increase of the temperature of solution preparation of these pillared clays drastically increases their activity for phenol oxidation. The Zr₄₀-Bent and The Zr₅₀-Bent show a higher activity than the corresponding Zr₂₅-Bent ones prepared under ambient temperature. With the Zr₄₀-Bent and The Zr₅₀-Bent, almost complete phenol conversion (98%) is reached in 1 h whereas the Zr₂₅-Bent leads to no more than 35% at the same time and complete conversion (90%) requires more than 2.5 h of reaction. When the solids were prepared at a temperature up to 50°C there was a decrease of the phenol conversion (Figure 2). The lowest activity and selectivity towards the formation of CO₂ and H₂O were achieved with the Zr₁₀₀-Bent clay (35%). This variation of activity among the different catalysts can be explained on the basis of their surface area and surface acidity. Amorphous samples (Zr₇₅-Bent and The Zr₁₀₀-Bent) have lower surface area and higher PZC as compared to the crystalline forms and therefore show lower catalytic activity.

Another trend is that the increased Zr content is linearly related with the increased reaction rate. The existence of Zr catalytic sites helps to enhance the interaction between the phenol and catalytic sites. After further comparison with the total acidity and surface area data, the catalytic activity is linearly. For example, Zr₄₀-Bent and The Zr₅₀-Bent have a higher total acidity and have the highest rate compared to Zr₇₅-Bent catalyst, with the most probable reason being the lower specific surface area with lower Zr content. In addition, increasing the Zr content enhanced the reaction rate due to the contribution of the ZrO₂ particles that act as active sites to generate •OH. The analysis of the effect of surface acidity on the radical mechanism indicated that the total acidity and L/B on the surface might be the main factors affecting the reaction rate. In fact, the adsorption-desorption mechanism is an important step in heterogeneous catalysis and is influenced by the intrinsic acidity of the solid catalyst [60,62].

TOC reduction is, in all the cases, significantly lower than phenol conversion indicating that oxidation of phenol proceeds through the formation of different intermediates and the final result is far from complete mineralization, namely oxidation to CO₂+H₂O. The maximum TOC reduction reaches 75% after 2 h in the case of Zr₄₀-Bent and Zr₅₀-Bent and close to 50% for Zr₂₅-Bent after 3.5 h, which means that significant amounts of intermediates still remain in solution. The Zr₇₅-Bent and Zr₁₀₀-Bent required 4 h to reach a plateau with a 40% and 34% of TOC conversion.

Various intermediate compounds such as catechol can be detected during the reaction showing that phenol oxidation reaction proceeds via well-known reactions [59,63,64]. According to the reaction pathway carried out by Devlin and Harris, the aromatic intermediates evolve to carboxylic acids, the distribution of which can be seen in Figure 3 [65]. In all the case, formic acid is the main product of this group of intermediates. In fact, the selectivity for formic acid is observed to be highest in all varied catalysts. Formic acid is more dominant in the product, showing a remarkable maximum concentration value and then a decrease due to mineralization. The trend for selectivity for a one product is similar to the trend observed by [64,66].

Conclusion

A Zirconium pillared bentonite with varied synthesis temperature has been prepared. It is found that synthesis temperature affects the physicochemical characteristics of material as shown by the zirconia crystal formation at higher Zr content, change in specific surface and porosity while total surface acidity and L/B ratio parameter are varied with temperature. Solids synthesized through this means are catalytically active in a reaction with high environmental impact; the reaction for the oxidation of phenol in diluted aqueous medium. The catalysts based on pillared clays prepared at a temperature under 50°C showed a higher activity for phenol conversion and TOC removal.

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