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Effect of Al and Ce on Zr-Pillared Bentonite and Their Performance in Catalytic Oxidation of Phenol[1]

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Abstract—Catalysts based on pillared clays with Zr and/or Al and Ce–Zr and/or Al polycations have been synthesized from a Tunisian bentonite and tested in catalytic oxidation of phenol at 298 K. The Zr-pillared clay showed higher activity than the Al-one in phenol oxidation. Mixed Zr–Al pillars lead to an enhancement of the catalytic activity due to the modification of the zirconium properties. The clays modified with Ce showed high conversions of phenol and TOC thus showing to be very selective towards the formation of CO_2 and H_2O.

Keywords: pillared clays, heterogeneous catalysis, catalytic oxidation in water, phenol, hydrogen peroxide

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1. INTRODUCTION

New environmental requirements provide significant challenges. Large volumes of wastewater are produced in chemical, petrochemical and pharmaceutical industries. Such wastewater contains organic contaminants which can be treated through homogeneous catalysts. Homogeneous catalysts 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. Different solids have been employed to catalyze the oxidation of organic compounds in wastewaters: Transition metal exchanged zeolites [1] and Cu^{2+}- or Fe^{3+}-montmorillonites have been proposed as active catalysts for organic compounds oxidation in aqueous phase [2]. Pillared interlayered clays (PILCs) have received increasing interest due to their textural and catalytic properties in different reactions [3]. PILCs or cross-linked clays are obtained by exchanging the interlayered cations of clay minerals with bulky inorganic polyoxocations followed by calcination. The intercalated polycations increase the basal spacing of the clay minerals, and after calcination, they are converted to metal oxide clusters by dehydration and dehydroxylation processes. These metal oxide clusters, named pillars, prevent the collapse of the clay mineral sheet structure. But, the inconvenience of pillared clay is the lack of stability at high temperatures. Thus many attempts have been made to improve the thermal stability of PILC. One appropriate way to overcome such a problem is the pillaring of clay minerals with solutions containing two different cations [4–8]. Another way to improve the distribution of the active phase and increase the catalytic properties of the PILCs is addition of cerium to the pillaring solution [9–12].

The aim of the present work is to prepare heterogeneous catalysts using natural clay as support. Those catalysts were tested in the phenol oxidation in aqueous medium, using H_2O_2 as an oxidant, in ambient conditions (298 K and atmospheric pressure).

We report in this paper the results obtained in the oxidation of an aqueous solution of phenol over simple Zr, Al, and mixed Ce–Al and/or-Zr-pillared bentonites prepared from zirconium tetrachloride. To our knowledge, the intercalation of clay minerals with zirconium oligomers using zirconyl chloride ($ZrOCl_2$) and zirconium acetate as the source of the polycations has been widely studied. Nevertheless, only one paper describing the pillaring of clay using zirconium tetrachloride ($ZrCl_4$) as precursor has been published [13].

2. MATERIAL AND METHODS

2.1. Starting Material and Solid Synthesis

The original clay is an interstratified illite/smectite obtained from Gafsa, Tunisia (noted G), homoion-

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ized with 1 M sodium chloride solution. This clay has been described in previous works [14–17]. In order to modify the clay mineral, different intercalated solutions are prepared. Zirconium tetrachloride was used as a source of zirconium polycation. $Al(NO_3)_3 \cdot 9H_2O$ was used in the synthesis of aluminum polycations. $Ce(NO_3)_3 \cdot 6H_2O$ was the source of cerium. The cerium molar percentage in all solutions was 20%. All solutions are prepared by slow addition of NaOH (0.2 M) to the solutions containing Zr, Al, Al–Zr, or Ce–Al–Zr-cations at room temperature until a specific pH. For Zr- and Ce–Zr-pillaring solutions this value was 2.8. It is the most widely used pH value for Zr-PILCs [18]. Al-and Ce–Al-pillaring solutions were adjusted to OH^-/Al ratio of 2 (pH 4.2) [6, 19, 20]. In the case of Zr–Al and Ce–Zr–Al solutions, pH of the solution was about 3.8 (near the pH corresponding to the simple Al-oligomer) and the solution remained clear. The obtained solutions were aged for 24 h at room temperature. The clay pillaring process is carried out through the ionic exchange of the previously aged solutions, keeping a ratio of 10 mmol of total metal per gram of clay. The intercalating solution is slowly added to a 2% clay aqueous suspension and then it was stirred for 24 h at room temperature. The solids were separated by centrifugation and washed by dialysis with distilled water. The final material was dried at 350 K, powdered gently in a mortar, and calcined for 2 h at 823 K at a heating rate of 275 K min^{-1}.

The samples are labeled in accordance with the nature of pillars (Zr, Ce–Zr, Al, Ce–Al, Al_x–Zr_y, and Ce–Al_x–Zr_y-bent). The subindex values indicate the metal percentage in the initial pillaring solution.

2.2. Characterization Methods

The X-ray diffraction (XRD) study was done on a Panalylitical X'Pert HighScore Plus device with CuK_α radiation.

N_2 adsorption-desorption experiments were carried out at 77 K on Quantachrome (USA) instrument. 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, V_t, was calculated at $P/P_0 = 0.99$. Before each measurement the samples were outgassed for 2 h at 403 K.

The chemical analysis of the starting material and modified samples was performed using AAS Vario atomic absorption spectrometer.

Cation exchange capacity (CEC) was determined by Kjeldahl 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 by Kjeldahl method. The CEC was expressed as mili-equivalent per gram of the calcined sample.

Brønsted and Lewis acid centers were determined by FT-IR spectroscopy on the basis of butylamine adsorption. *n*-Butylamine solution in cyclohexane (10 mL) was added to 0.1 g of the catalyst. The mixture was shaken at room temperature. After drying, each sample was calcined at a different temperature. FT-IR spectra were recorded in the region 1800–400 cm^{-1} on a Perkin-Elmer spectrometer using the KBr pellet technique.

Thermogravimetric analysis (TGA) was done between room temperature and 1100 K on a Perkin-Elmer TGS-2 instrument in air (35 cm^3/min) at a heating rate of 10°C min^{-1}. The sample weight was 0.050 g.

2.3. Catalytic Study

The catalytic oxidation of phenol in a diluted aqueous medium was carried out in a 250 mL batch glass reactor open to atmosphere and thermostatted at 298 K with stirring and constant monitoring of pH. The device featured an automatic reagent dosing unit (Dosimat 725 Metrohm) for the continuous addition of hydrogen peroxide solution. For each test the reactor was loaded with 100 mL of a phenol solution (2.00 g/L) and 0.5 g of catalyst. The high purity hydrogen peroxide solution (10.00 g/L) was added at a 2 mL/h rate. The pH was continuously adjusted to 3.7 and an air flow was introduced in the reactor at a volume rate of 2 L/h. Samples from the reaction medium were taken at initial time and after 15 and 30 min, and then at each hour until completing 5 h experiment. The catalyst was removed from the samples using a 0.2 μm nylon filter. The samples were analyzed immediately after taken. 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 600E liquid chromatograph 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.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Pillared Clays

3.1.1. XRD. Table 1 lists the basal spacing of PILCs with single and mixed oxide pillars after calcination at 823 K. As a reference, basal spacing of the purified clay calcined at the same temperature was shown as well. As shown in Table 1, the basal spacing increases from 10 to 17–20.5 Å. This fact indicates that the mineral was successfully pillared in all cases. Depending on the kind of hydroxycation used as a pillar, the pillaring process leads more or less to an increase in the interlayer spacing. The PILCs showed different

Table 1. Basal spacings, (after calcination at 823 K), micropores volume, and specific surface areas of the starting and pillared clays

	d_{001} (Å)	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	$V\mu$p ($\mathrm{cm^3\,g^{-1}}$)
Na-Bent	10	107	0.021
Zr-Bent	18.2	200	0.063
Ce–Zr-Bent	19.3	180	0.025
Al-Bent	17.4	191	0.062
Ce–Al-Bent	18.7	123	0.024
$Al_{50}Zr_{50}$-Bent	19.2	162	0.046
Ce–$Al_{50}Zr_{50}$-Bent	19.1	121	0.023
$Al_{10}Zr_{90}$-Bent	20.5	177	0.054
Ce–$Al_{10}Zr_{90}$-Bent	20.5	123	0.021

Table 2. Chemical analysis and cationic exchange capacity of the starting and the pillared clays

	CEC (meq/100g)	Al, %	Zr, %	Ce, %
Na-Bent	78	24.80	0	0
Zr-Bent	24	20.34	16.71	0
Ce–Zr-Bent	22	20.18	16.57	0.55
Al-Bent	43	34.60	0	0
Ce–Al-Bent	32	34.11	0	0.42
$Al_{50}Zr_{50}$-Bent	27	26.48	17.31	0
Ce–$Al_{50}Zr_{50}$-Bent	26	26.11	16.96	0.30
$Al_{10}Zr_{90}$-Bent	25	25.05	20.98	0
Ce–$Al_{10}Zr_{90}$-Bent	23	24.97	20.88	0.41

increases of basal spacing: 18.2 Å for Zr-PILC, 17.4 Å for Al-PILC, 19.2 for $Al_{50}Zr_{50}$-PILC, and 20.5 Å for $Al_{10}Zr_{90}$-PILC. Notice that the interlayer spacings of PILCs with mixed oxide pillars of Zr and Al are higher than that of PILCs with single oxide pillars of either Zr or Al. The incorporation of Al leads to an increase in the basal spacing with greater value for $Al_{10}Zr_{90}$-bent. Added to the enhancement of the basal spacing, the addition of Al was found to provide a useful way to improve the structural properties of the Zr-PILC. In fact, the structure of mixed Al–Zr-PILCs is well-ordered and remains stable after calcination at 823 K, and this is not evident for the Zr-PILC sample which shows a wider peak [15]. The broadness of the 001 diffraction peak in the case of Zr-PILCs is widely reported in the literature [21, 22] The addition of cerium to the aluminum and zirconium intercalated solution produces an enhancement of the basal spacing from 17.4 to 18.7 Å for Al-bent and from 18.2 to 19.3 Å for Zr-bent. However, no considerable differences were observed in the basal spacing value of the Ce–Al–Zr-PILC and Al–Zr-PILC samples (Table 1). Besides, the introduction of cerium has a beneficial effect on the structural properties of Al–Zr-PILCs [15], indicating that the addition of Ce is likely to provide favorable conditions for the formation of the Zr and/or Al pillar, providing greater thermal resistance [8, 23–26].

3.1.2. S_{BET}. The surface area and micropore volume values of the studied solids (Table 1) are in agreement with the X-ray diffraction results, revealing an increase in the surface area of the purified bentonite after the pillaring process in all samples, which is corresponding to the successful pillaring of the clay and the consequent formation of microporous structures.

BET surface area and micropore volume of the single pillared clay Zr- and Al-pillared clays are higher than that of the mixed Zr–Al pillared clay. The same observation is noted in previous works dealing with the mixed Al/Zr, Al/Fe, and Al/Cr [7] and mixed Zr–V [27]. Incorporating cerium resulted in a decrease in specific surface area and micropore volume. It has been reported in the previous literature that the specific surface area and the pore volume of pillared clay decrease after addition of cerium [23, 28–30].

3.1.3. Chemical composition. The chemical composition shows that Al content of clays modified with solution containing Al cation are higher than that of purified bentonite (Table 2), indicating it effective introduction in the material. The amount of zirconium taken up by the clay in the presence of aluminum was larger than the amount taken up by the clay in the case of simple Zr-pillared clay. In fact, the ZrO_2 percentages are 16.71, 17.31, and 20.98% for the Zr-bent, $Al_{50}Zr_{50}$-bent and $Al_{10}Zr_{90}$-bent samples respectively. This indicates a modification of the zirconium pillar by hydrolysis and/or polymerization [15]. In the case of samples modified with cerium, the introduction of cerium in the samples is revealed, showing a practically greater value in solids modified with the simple system Ce–Al (0.42%) or Ce–Zr (0.55%), while materials modified with mixed system Ce–Zr–Al show values of 0.41 and 0.30%, respectively for Ce–$Al_{10}Zr_{90}$-bent and Ce–$Al_{50}Zr_{50}$-bent samples. The same behavior was observed in [31]. Much less Ce was incorporated into the pillars than originally present in the solution. [32, 33] observed the same behavior when pillaring a bentonite with Ce–Al polycation and suggested that this low amount of cerium could be explained from the structure proposed for the Al–Ce polycation, different from the simple structure for the Keggin ion [8, 27] in which a Ce atom in tetrahedral coordination is surrounded by four Al_{13} units, giving the possibility of generating pillars with a low Ce content.

3.1.4. Cation exchange capacity. The CEC of all pillared samples decreases compared to the CEC of parent clay mineral. The low values of CEC after pillaring (Table 2) suggest the irreversibility of cationic exchange. The residual exchange capacity of Zr-bent is lower than that of Al-bent. This shows that zirco-

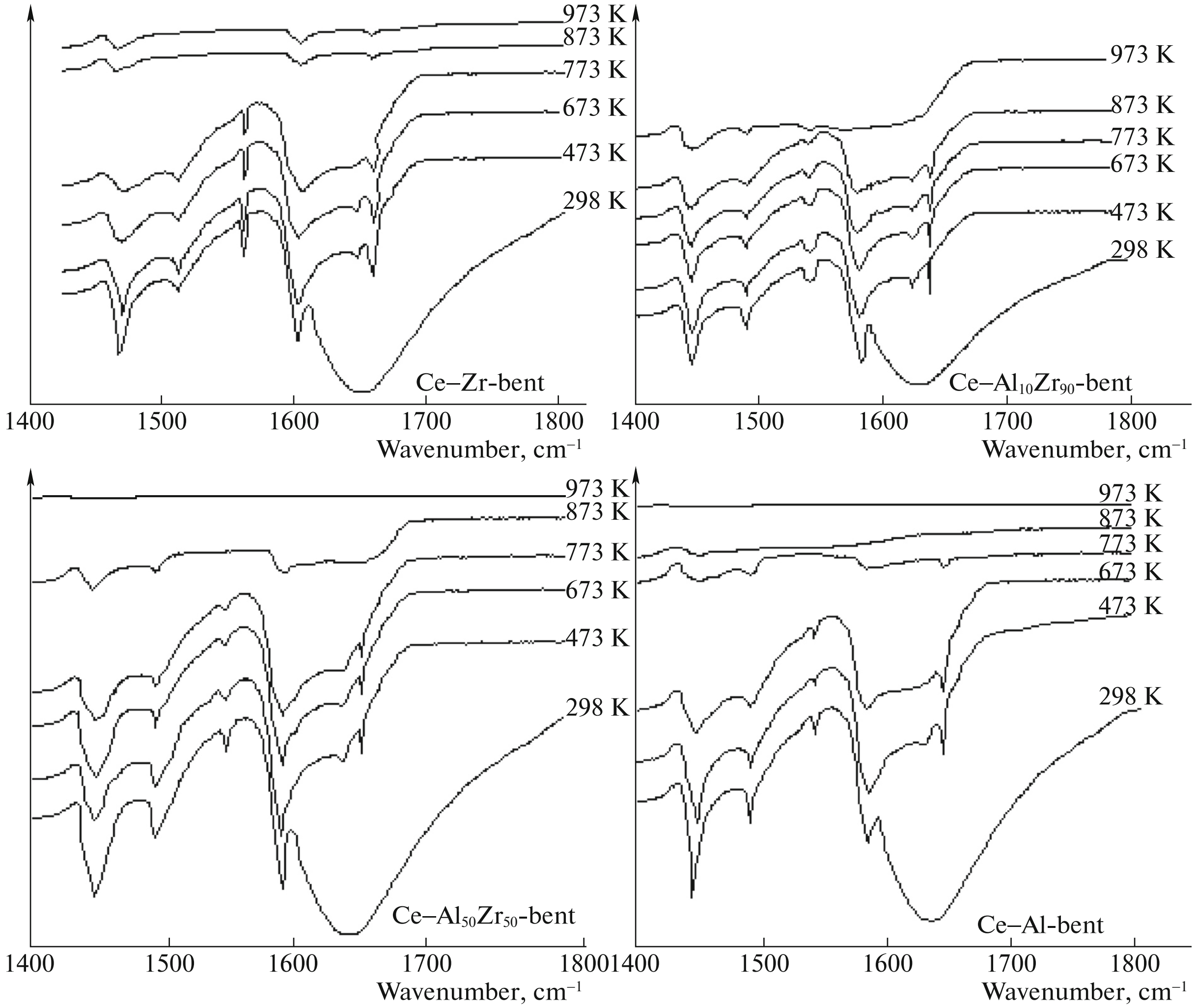

Fig. 1. FT-IR spectra of *n*-butylamine adsorbed on Ce-modified PILCs.

nium polyhydroxycations are more efficient in blocking negative charge than Al ones. The incorporation of cerium leads to a slight decrease in the CEC value in all pillared samples. This decrease is more pronounced in the case of Al-PILC.

3.1.5. Surface acidity. The surface acidity of original clay and Zr-and/or Al-PILCs evaluated from IR study of *n*-butylamine adsorbed on synthesized solids, has been described in previous works [16]. The results of surface acidity measurements indicated that:

(i) the modified forms of clay exhibit better Brønsted and Lewis acidity compared to their starting form (the Na-bent sample) which presents only weak Lewis acid sites at 298 K;

(ii) Zr pillars leads to stronger acidity than Al pillars;

(iii) the Zr–Al-PILC samples show the presence of both Brønsted and Lewis acidity in high concentrations.

The IR spectra of *n*-butylamine treated Ce–Zr- and/ or Al-PILC at the temperature ranging from 298 to 973 K are presented in Fig. 1. The addition of the cerium leads to the appearance, in all samples, of a new IR band at 1638 cm^{-1} corresponding to Brønsted acid sites [34]. Then, the bands assigned to *n*-butylamine coordinated onto Brønsted acid sites (1540 cm^{-1}) in the case of Ce–Al-bent remains after evacuation at 673 K. Thus suggests the stronger nature of the Brønsted acid sites when compared to the Al-PILC. This result indicates that cerium improves the Lewis and Brønsted surface acidity. Similar behavior was observed in [26]. Finally, the intensities of the bands assigned to *n*-butylamine coordinated onto Lewis and Brønsted acid sites are slightly reduced in all samples after thermal treatment.

3.1.6. TGA analysis. TGA curves of the neat and Al- and/or Zr-pillared clays are shown in Fig. 2. The TGA curves for cerium modified pillared clays were also examined to identify the role of the cerium on the

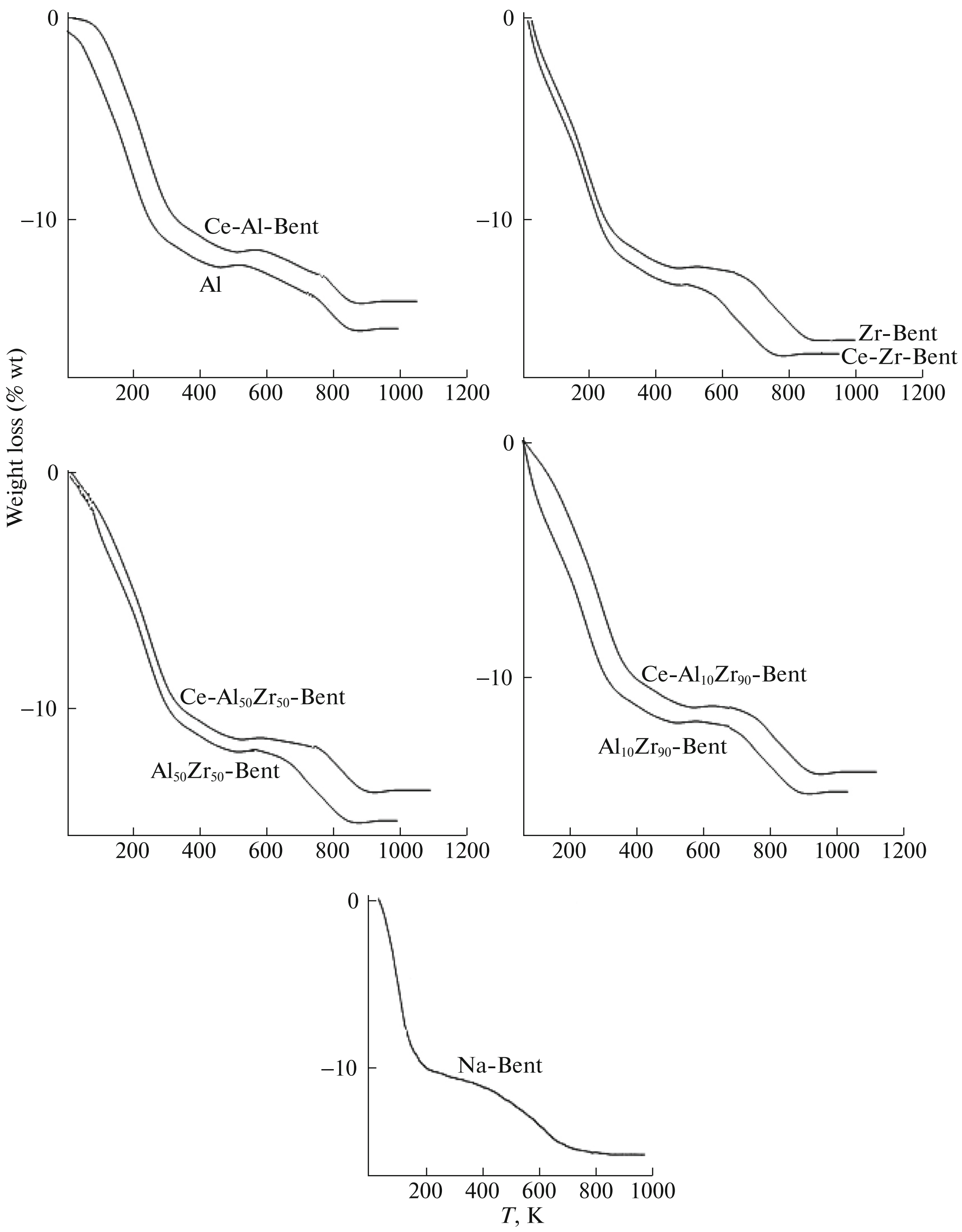

Fig. 2. TGA curves for initial and modified clays.

surface of the clays and are given in Fig. 2. For all samples, the weight loss occurs in two steps. In the case of the natural clays, two temperature ranges can be distinguished. The first, up to about 473 K, can be ascribed to the elimination of hydration water. The second, about 700 K, can be associated to the dehydroxylation of the clay sheets. For all modified clays, the weigh losses took place in two steps. The first step corresponds to the desorption of surface water physically adsorbed from 298 to 473 K, whereas the second one occurs between 673 and 973 K assigned to either the dehydroxylation of the clay structure and the pillar species incorporated after pillaring. As shown in Fig. 2, however, there is a slight but visible dissimilarity in the TGA peak of each material. For example, Al-PILC gives the TGA peak at 853 K, but for Zr-PILC

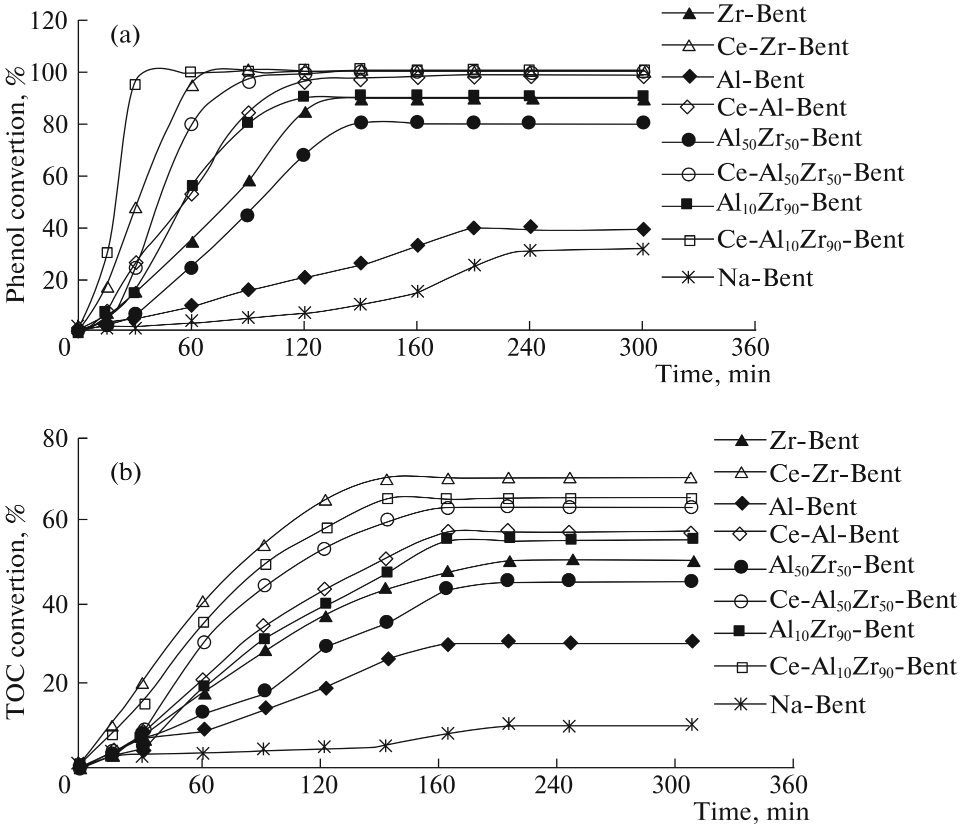

Fig. 3. Catalytic activity of different catalysts in the phenol oxidation (a) and TOC (b) conversion in diluted aqueous medium at atmospheric pressure and at 298 K.

this peak is at 673 K. The TGA results of mixed Al–Zr samples show a weight loss at about 878 K. The difference observed in the dehydroxylation temperature can be due to the difference in the thermal stability of the synthesized materials. However, the TGA peaks for samples containing cerium are observed at around 883 K for all samples. This suggests that the introduction of the cerium to the pillared clay may lead to a shift of the dehydroxylation temperature to a higher temperature region, which can be related to the improvement of the thermal stability observed for the cerium modified materials.

3.2. Activity of the pillared clays in CWPO of phenol. Solid material prepared via pillarization of the Tunisian bentonite with Zr and/or Al, Ce–Zr and/or Al polycations possess excellent catalytic properties in the phenol oxidation reaction. Likewise, considerable activity is found in the TOC mineralization (Figs. 3a and 3b). In Fig. 3a, which shows the phenol conversion as a function of the reaction time for the six modified solids and the natural clay. We can observe that the starting purified clay (Na-bent) used in this catalytic reaction is quite active. Calcined Na-bent reached only 31% conversion of phenol after 4 h of reaction. The non-negligible catalytic activity obtained for calcined purified clay can be explained by the initial contents of iron oxides found in natural clay (8.03%) [33]. The materials modified with Zr species show better results than the solids modified with Al species. The conversion observed with the clay modified only with aluminum is ascribed to the iron species found in the octahedral layers of these materials, as established in previous works [27–30, 32–35]. As already mentioned, it has been found that $Al_{10}Zr_{90}$-bent sample shows better phenol conversion than $Al_{50}Zr_{50}$-bent. The highest activity was achieved with the clays modified with higher amounts of Zr (Zr-bent and $Al_{10}Zr_{90}$-bent).

On the other hand, it is important to mention that the use of cerium allows to increase the activity of the obtained catalysts in phenol oxidation up to 100% conversion within the first 2 h of the reaction. In fact, after comparing the results with those obtained without Ce, the enormous catalytic potential of these materials once they have been modified via pillaring with mixed Ce–Zr and/or Al systems is evident, since for the clay modified with Zr and Zr–Al the conversion was 88% after 2.5 h, for Al-modified clay it was 40% after 3 h, as compared to 100% conversion for all samples with cerium. In all the experiments with (Zr-and/or Al-PILCs, Ce–Zr-and/or Al-PILCs) modified clays, leaching of cerium, zirconium or alu-

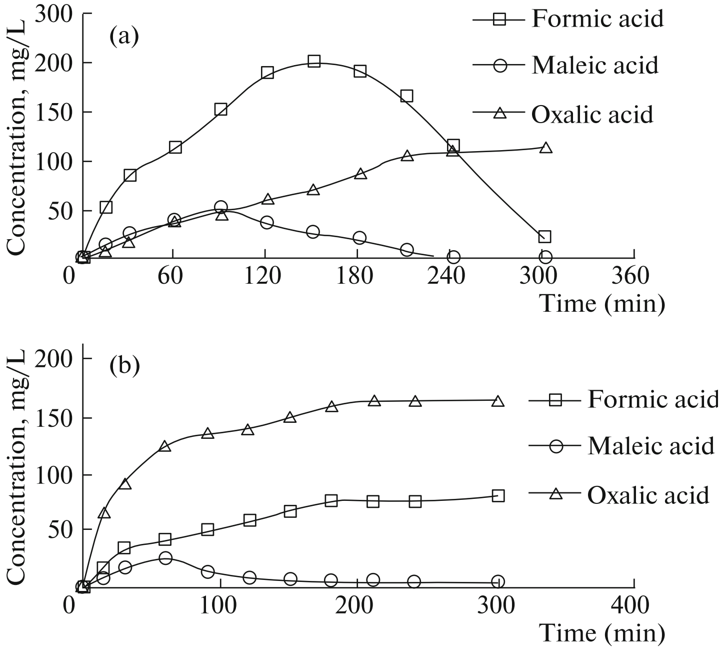

Fig. 4. Time-evolution curves of aromatic intermediates from phenol with pillared clays; (a) Zr-bent, (b) Al-bent.

minum species was very low (0.01 ppm for Ce, 0.04 ppm for Zr, and 0.05 ppm for Al).

TOC conversion levels (Fig. 3b) follow the same tendency as phenol conversion. Regarding the TOC conversion reaction (Fig. 3b), the favorable effect of the cerium addition can also be observed. Enhancement of the catalytic activity in oxidative reactions is due to the oxygen storage capacity of cerium oxides. Similar results were observed in [20, 36, 37].

According to the reaction pathway described in [38], phenol conversion at first step leads to aromatic intermediates like hydroquinone and benzoquinone. These intermediates are then converted to carboxylic acids. The kinetic curves for carboxylic acids formation are presented in Fig. 4. Some important differences can be pointed out among the different pillared clays. In the case of Zr-PILCs, formic acid is the main product of this group of intermediates, showing a remarkable maximum concentration value and then a decrease due to mineralization. In the case of Zr-bent sample, the TOC conversion reaches its maximum level after 200 min (Fig. 3b), although the phenol conversion is 85% (Fig. 3a) from lower time (150 min) and at this time the formic acid concentration did not finish its mineralization clays (Fig. 4a), in agreement with the result reported by other authors [39]. This trend is not observed in the case of Al-PILCs, suggesting that whether mineralization is not taking place or it is balanced by formic acid formation from other carboxylic acids in the reaction pathway. The main carboxylic acid in the case of Al-PILCs is oxalic. $Al_{50}Zr_{50}$-Bent and $Al_{10}Zr_{90}$-bent samples show the same behavior as Zr-PILCs. And, as in the case of sample modified without cerium, the time-evolution curves of carboxylic acids also suggest a refractory behavior in the experiments carried out with the Ce–Zr and/or Al-bent catalyst (not shown in Fig. 4). In fact, the main carboxylic acid in the case of Ce–Al-PILCs is oxalic. And in the case of Ce–Zr-and Ce–Zr–Al-PILCs, formic acid is the main product of this group of intermediates.

From the above results, the addition of Ce shows excellent performance. In order to discriminate between homogeneous and heterogeneous oxidation, several experiments were done in similar conditions with soluble cerium species. In this way, subsequent investigations of the catalytic activity of the clay modified with only Ce without Al and Zr is assessed. To investigate the performance of cerium, the starting clay is exchanged 4 times with 0.4 M $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution at 25°C for 24 h. In the same conditions, the Ce-modified bentonite used in this catalytic reaction is quite inactive (6% conversion of phenol and 0% conversion of TOC after 20 h). This correlate well with the result obtained through chemical analysis and XRD patterns. In fact XRD analysis show that there is an increase in the basal spacing from 12 to 14.3 Å upon insertion of cerium ions in the parent clay which is attributed to the larger hydration sphere surrounding the Ce ions in the interlayer. When calcined at 823 K, Ce-bentonite sample shows collapse of the layered structure. Besides, the chemical analysis data of this solid after dispersing in the NaCl solution (1 M) shows that about total of cerium is detected in the solution of NaCl. This amount is removed by exchanged reaction. So the phenol oxidation reaction is catalyzed by heterogeneous catalyst and the homogenous part fails to oxidize the phenol.

4. CONCLUSIONS

Several Zr and/or Al and Ce–Zr and/or Al pillared Tunisian clays are prepared. Modification of bentonite with these polyhydroxycations is a convenient method of preparation of pillared solids. The catalysts obtained by Zr or Zr–Al polyhydroxycations pillaring are highly efficient for the phenol oxidation reaction in diluted aqueous medium at very mild conditions (298 K and atmospheric pressure). The stability of the active phase of these catalysts is evident, showing extremely low metal leaching.

The addition of Ce during the synthesis of the catalysts leads to an increase of its activity in oxidation of phenol and of the formed intermediate compounds and is beneficial for the total oxidation (mineralization) reaction. Finally, the activity of the catalysts is found to increase with its acidity, which is related to the Zr content and to the presence of cerium.

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