

Catalytic wet peroxide oxidation of phenol over Ce-Zr-modified clays: Effect of the pillaring method

Saida Mnasri-Ghniemi^{*,†} and N. Frini-Srasra^{*,**}

^{*}Laboratoire de Physico-chimie des Matériaux Minéraux et Leurs Applications,
Centre National des Recherches en Sciences des Matériaux, Technopole Borj Cédria, BP 95-2050 Hammam Lif, Tunisia

^{**}Départements de Chimie, Faculté des Sciences de Tunis, 1060 Tunis, Tunisia

(Received 13 April 2014 • accepted 14 July 2014)

Abstract—Preparation, characterization and catalytic activity of Zr- and Ce-Zr pillared clays with different method (direct, indirect, and under reflux), starting from Tunisian interstratified illite-smectite bentonite, are described. Zirconium pillared clays (Zr-PILC) revealed weaker thermal stability. To overcome this drawback, the addition of cerium (Ce) as the second metal component to Zr-PILC was attempted. Wet peroxide oxidation of phenol from industrial wastewaters was carried out over these catalysts. The catalysts were very efficient in the phenol oxidation reaction in diluted aqueous medium under mild experimental conditions (298 K and atmospheric pressure). The addition of Ce in the synthesis step of the inorganic polycations yielded a favorable effect on the pillaring of the materials, allowing the increase of the basal spacing and enhancing the catalytic activity of the solids. The pillared clays were characterized by XRD, chemical analysis, CEC, and N₂ adsorption to 77 K. The acidity of the pillared clays was calculated from the adsorbed n-butyl amine.

Keywords: Pillared Clays, Zirconium, Cerium, Catalysis, Phenol Oxidation

INTRODUCTION

Great efforts are being made worldwide to enforce strict control on wastewaters from household, agricultural and industrial activities, which in many instances contain highly toxic organic compounds in diluted form. Phenol is one of the most important representatives of organic pollutants generated by industrial processes, due to its high toxicity even at low concentrations; and when present in natural waters it can lead to the formation of substituted phenols during chlorine disinfection processes. These kinds of pollutants can be removed using processes like advanced oxidation, membrane processes, adsorption, and anaerobic/aerobic biological processes [1].

Pillaring of clay with inorganic polycation to prepare thermally stable rigid cross-linked materials of uniform micropores and acidity offers an important line of research in obtaining solids responding to the CWPO process. In fact, since the first report on this type of material was made at the end of the 1970s [2], a considerable number of studies have been carried out to search for materials able to be active in catalysis and other applications. However, the use of pillared clays in commercial catalytic processes has been limited due to their restricted thermal stability. One of the options that have been tested to solve this inconvenience and to improve the catalytic properties of PILCs is the addition of a second metal to the pillaring solution to improve the stability, activity and selectivity of the mixed system. The interaction of the second cationic com-

ponents with the pillars in the microenvironment of the clay is very crucial for the property of the solid. Indeed, it has been shown that pillared clay with different basal spacing and microporosity was prepared with mixed cation pillaring [3-7]. In addition, previous works [7,8] report that the incorporation of species of Ce favors catalytic activity (CWPO reaction) of the pillared clays, probably because the cerium oxide formed in the solids enhances the textural properties of the solid, the dispersion and/or the redox properties of active species [9,10].

One of the essential parameters in the preparation of pillared clays is the mode of the preparation both for pillaring solutions and during the intercalation process. In the past few years, several techniques have been tested to facilitate and increase the incorporation of polyhydroxocations within the structures of these solids, including microwaves, ultrasound, and reflux, among others.

Throughout this work, the synthesis of Zr- and Ce-Zr-pillared clays and their catalytic evaluation in the phenol oxidation reaction are carried out, emphasizing the synthesis and characterization of modifying solid species from Zr and Ce-Zr-polyhydroxocationic solutions.

METHODS AND MATERIALS

1. Materials

The starting material used in this work was a purified interstratified illite/smectite (G) that was obtained from Gafsa, southwest of Tunisia. This bentonite has been thoroughly characterized in previous works [11-14]. The impurities are mainly quartz and calcite. The chemical weight percent composition of this bentonite was: SiO₂ 61.38, Al₂O₃ 24.80, Fe₂O₃ 8.03, Na₂O 3.06, MgO 1.38, CaO

[†]To whom correspondence should be addressed.

E-mail: saidamnasri@gmail.com

Copyright by The Korean Institute of Chemical Engineers.

0.13, K₂O 1.40. The average elemental formula determined from the Na-exchanged purified fraction was [Si_{7.43}Al_{0.57}][Al_{2.96}Fe_{0.73}Mg_{0.24}]O₂₀(OH)₄Na_{0.71}K_{0.21}Ca_{0.01}. The homoionic material employed in the present study has a S_{BET} = 107 m²g⁻¹, $V_{\mu p}$ = 0.021 cm³g⁻¹, d_{001} = 12 Å and contains a cation exchange capacity (CEC) of 78 meq/100 g clay.

2. Methods of Preparation

2-1. Pillaring Solutions

Zirconium tetrachloride (ZrCl₄) is used as a source of zirconium polycations. The source of cerium was Ce(NO₃)₃·6H₂O. Pillaring solutions of Zr or Ce-Zr cations were prepared by slowly adding a basic solution (NaOH 0.2 M) to the corresponding cationic solution (0.1 M) under constant stirring at room temperature until a pH equals 2.8. The obtained solution was aged under stirring at room temperature for 24 h.

2-2. Pillaring Methods

Three methods are used:

- A classical method, called 'D' where the pillaring solution and the clay suspension (1% w/w) are prepared separately and then the pillaring solution is slowly added to the diluted clay suspension.
- An inverted method to the previous one, called 'I' where the dry clay powder is directly dispersed in the diluted pillaring solution.
- A third method called 'DR' where a previously refluxed solution is added dropwise to the clay suspension.

The pillaring process was developed by ionic exchange of the bentonite clay with the Zr-polyoxocation solution at 298 K, adding the pillaring solution (dropwise) to a clay suspension (2%); the clay was previously swelling for 2 hours. After addition, the mixture was left in continuous stirring for 24 hours at the same temperature. Finally, the resulting products were separated from suspension by centrifugation and washed by dialysis with distilled water. The final material was dried at 350 K and calcined for 2 h at 823 K.

PILCs are labeled as following:

Ce-Zr_{method}-bentonite.

3. Characterization Methods

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 77 K on Quantachrome, USA instrument. The N₂ 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 determined by atomic adsorption, the spectrometer used was of 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 Kjeld-

hal. The CEC is expressed as milli-equivalent per gram of the calcined sample.

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 cyclohexane solution was added to 0.1 g of catalyst. The mixture was shaken at room temperature. After drying, each sample was calcined at different temperature. FT-IR spectra were recorded in the region 1,800-400 cm⁻¹ on a Perkin-Elmer infrared Fourier transform spectrometer using the KBr pellet technique.

4. Catalytic Study

Preliminary catalytic experiments were carried out at room temperature using 0.5 mM of catalyst in a 100 ml of aqueous phenol solution (5×10^{-4} M) in a batch reactor. The oxidant reagent, H₂O₂ (0.5 M) was added in excess. The percent of total organic carbon (% TOC) weakening was determined using a Dohrman DC80 carbon analyzer, which measures the nondegraded and residual phenol.

RESULTS AND DISCUSSION

1. Characterization of the Pillared Clays

1-1. X-ray Diffraction

XRD patterns of samples obtained by Zr-bentonite after calcination at 823 K obtained with different methods, with and without doping of cerium (Fig. 1), revealed that the d_{001} value of the obtained peaks is enhanced. The results indicate that the modification carried out on the clay leads, in the cases of 'D' and 'I' method, to the successful pillaring of the material. In fact, the shift of the d_{001} basal spacing from 12 Å (starting clay) to 15-18 Å confirms the modification via pillaring. However, in the case of the intercalation of the Na-clays with zirconium polycations under the reflux conditions, it must be emphasized that this method results in the total delamination of the clay structure, which becomes disordered, thus giving products on which the (001) reflection peaks disap-

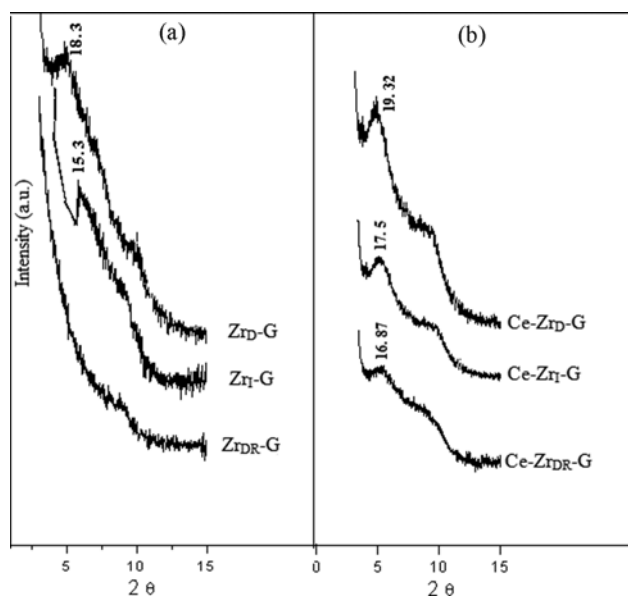


Fig. 1. X-ray diffractograms of different pillared clays calcined at 823 K.

pear. Similar results have been reported in earlier studies using montmorillonite [15] and saponite [16], which explains the degradation of the clay structure by the quick drop of pH to low values of $\text{pH} < 1$. However, in the present case, the pH of the intercalated solution remained the same ($\text{pH} = 2.8$) irrespective of the method applied, whereas the destruction of the clay structure was detected only for the samples prepared by the DR method.

Concerning Ce-Zr-bentonite samples (Fig. 1(b)) using 'D' and 'T' method, the d_{001} reflection for basal spacing was very intense and the intensity was higher in those samples than on Zr-bentonite (Fig. 1(a)), which indicates cerium oxides are still present in the Zr-pillared clay and remodel the order of the layered structure. The most striking result is that, the introduction of cerium in the Zr-pillaring solution using 'DR' method has a beneficial effect in the crystallinity of the resulting materials. In fact, Fig. 1(b) reveals that, the $\text{Zr}_{\text{DR}}\text{-G}$ sample shows a delaminated peak. This is not evident for the Ce- $\text{Zr}_{\text{DR}}\text{-G}$ sample which presents a sharp (001) peak. The structure is ordered and remains stable after calcination at 823 K. The improvement of crystallinity in the case of Ce- $\text{Zr}_{\text{DR}}\text{-G}$ shows that favorable conditions are met to form zirconium pillars by refluxed treatment because of the presence of cerium. So, the cerium incorporation in the case of 'DR' method allows the synthesis of zirconium pillars without delamination. Finally, no characteristic XRD signal of chemical species from cerium was observed, probably due to the incorporation of relatively too small quantities to be detected by X-ray diffraction in a clay matrix.

1-2. Cation Exchange Capacity

The residual cation exchange capacity (CEC) can be used as a tool for measuring the intercalated pillar linked to the sheet of clay. The CEC of pillared samples decreases compared to the CEC of the parent clay (Table 1). This shows that the oligomers are irre-

versibly fixed to the clay layer on heat treatment. The residual exchange capacity of $\text{Zr}_D\text{-G}$ and $\text{Zr}_T\text{-G}$ is lower than the $\text{Zr}_{\text{DR}}\text{-G}$. The incorporation of cerium leads to a slight decrease in the CEC value in all pillared sample. This decrease is more pronounced in the case of Ce- $\text{Zr}_{\text{DR}}\text{-G}$. The decrease in cation-exchange capacity of samples saturated with cerium was partially attributed to the migration of the cerium ion to octahedral sites of the 2:1 layers. Similar trends have been reported [17].

1-3. Chemical Analysis

Chemical analysis data (Table 2) indicates that 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 the three solids after dispersing in the NaCl solution (1 M) showed that only in the case of sample prepared with 'DR' method is there an exchange of zirconium species with Na^+ cations. In fact, with this sample 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 ($\approx 47 \text{ meq/100 g}$) (see Table 1).

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 $\text{Zr}_D\text{-G}$ (0.58%), while materials modified with mixed system $\text{Zr}_T\text{-G}$ and $\text{Zr}_{\text{DR}}\text{-G}$ show value of 0.30% and 0.37% respectively.

Besides, the effect of Ce on the pillared clay is much greater in the case of sample prepared with 'DR' method than in the case of sample prepared with 'D' and 'T' ones. The chemical analysis data of the (Ce- $\text{Zr}_{\text{DR}}\text{-G}$) solid after dispersing in the NaCl solution (1 M) showed that a negligible amount of zirconium was detected in the solution of NaCl (0.02%). So the cerium incorporation helps the formation of a stable Zr oligomer using the refluxed method. This result is further confirmed by the XRD data (Fig. 1).

1-4. Textural Properties

The intercalation produced significant microporosity and reduced the mesoporosity in the original sample (Table 3). 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. We emphasize here that, despite the failure of the pillaring process in the case of the $\text{Zr}_{\text{DR}}\text{-G}$, this sample offers surface areas and porosities, similar to the $\text{Zr}_D\text{-G}$ one. In a previous work Occelli [18] showed that delamination is

Table 1. Cationic exchange capacities of different samples

Samples	CEC (meq/100 g)
Na-G	78
$\text{Zr}_D\text{-G}$	24
$\text{Zr}_{\text{DR}}\text{-G}$	47
$\text{Zr}_T\text{-G}$	23
Ce- $\text{Zr}_D\text{-G}$	22
Ce- $\text{Zr}_{\text{DR}}\text{-G}$	23
Ce- $\text{Zr}_T\text{-G}$	23

Table 2. Chemical composition of the pillared clays

	ZrO_2 (%)	* ZrO_2 (%)	** ZrO_2 (μmol)	CeO_2 (%)	* CeO_2 (%)	** CeO_2 (μmol)
$\text{Zr}_D\text{-G}$	16.71	16.54	17	0	0	0
$\text{Zr}_T\text{-G}$	13.42	13.36	17	0	0	0
$\text{Zr}_{\text{DR}}\text{-G}$	28.45	16.20	9.9410 ³	0	0	0
Ce- $\text{Zr}_D\text{-G}$	16.57	16.53	11	0.58	0.56	0.10
Ce- $\text{Zr}_T\text{-G}$	13.39	13.38	15	0.30	0.25	0.15
Ce- $\text{Zr}_{\text{DR}}\text{-G}$	16.15	16.13	13	0.37	0.32	0.13

*Percentage of Ce or Zr After exchange with NaCl (1 M)

**Leachate Ce or Zr, after reaction, in the medium

Table 3. Textural properties of different samples

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{ext} ($\text{m}^2 \text{g}^{-1}$)	S_{mp} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$)	V_{mp} ($\text{cm}^3 \text{g}^{-1}$)
Na-G	107.2	67.5	39.7	0.15	0.02
Zr _D -G	199.5	77.3	122.2	0.21	0.06
Zr _I -G	187.1	68.7	118.4	0.19	0.06
Zr _{DR} -G	190.6	65.7	124.9	0.18	0.06
Ce-Zr _D -G	180	85	95	0.20	0.025
Ce-Zr _I -G	178	87	91	0.20	0.024
Ce-Zr _{DR} -G	179.5	80	99.5	0.20	0.024

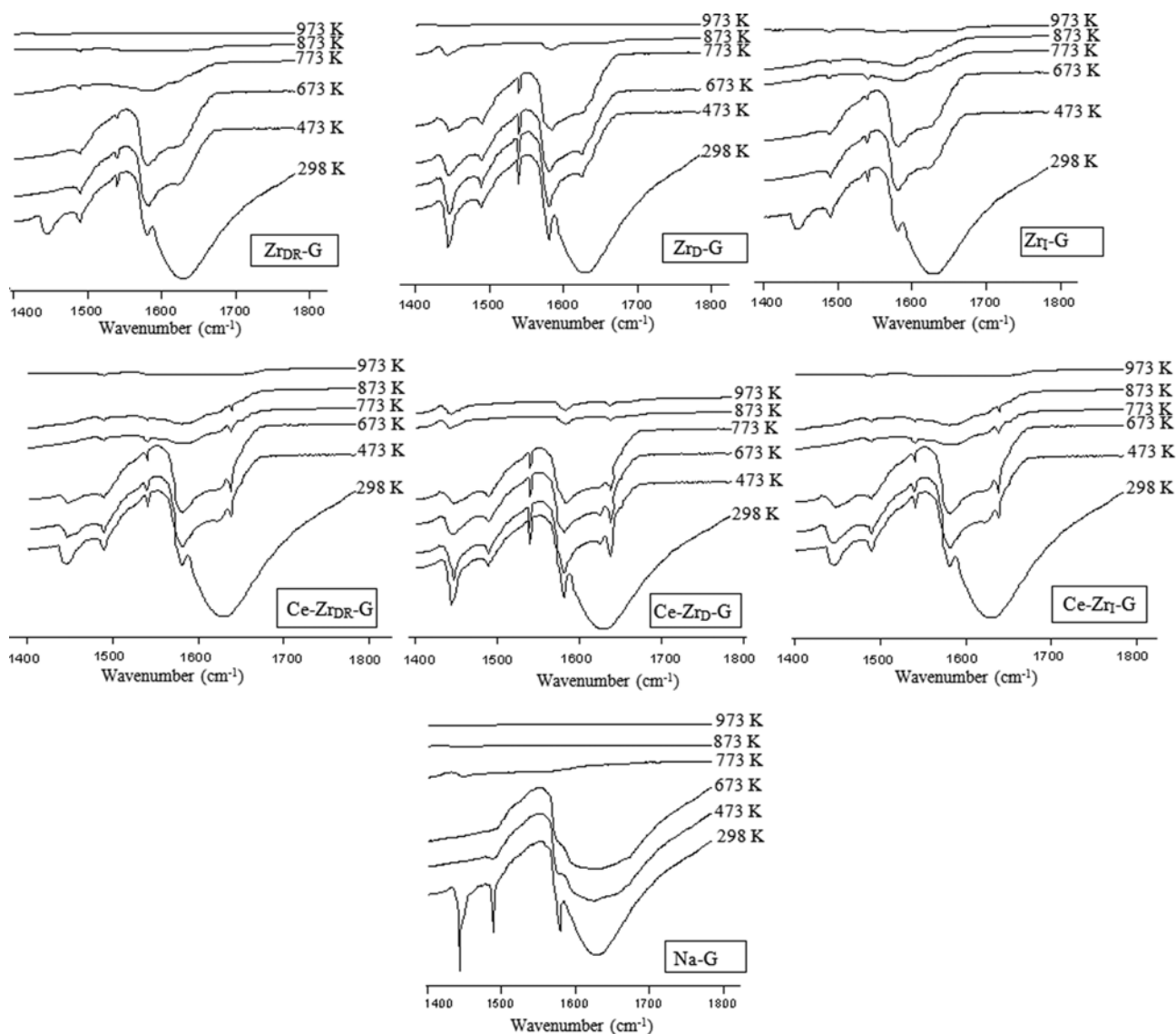
S_{ext} : external surface; S_{mp} : microporous surface; V_p : microporous volume

characterized by a house-of-cards-like structure, which increases the mesoporosity accompanied by a certain microporosity in an FF (face-to-face) short-range association coming from pillaring,

which gives rise to the disordered structure shown by XRD measurement (Fig. 1). Incorporating cerium resulted in a slight decrease in specific surface area and micropore volume. The loss of microporosity proved that the Ce^{3+} with a large radius entered into the clay layer and resulted in pore blocking [19]. Previous literature reported that the specific surface area and the pore volume of pillared clay decrease after addition of cerium [19-22]. In the present case, to explain the slight decrease in specific surface area and micropore volume, we suggest a substitution of Zr^{4+} cation with Ce^{3+} cation instead of pore blocking by cerium, keeping in the mind that those cations have similar ionic radius (0.087 nm for Zr^{4+} and 0.102 nm for Ce^{3+}).

1-5. Surface Acidity

The infrared spectra of n-butylamine adsorbed on the starting bentonite and all modified samples after evacuation, at 298-973 K (Fig. 2) showed five bands at 1,445, 1,490, 1,540, 1,590, and 1,623 cm^{-1} . According to [23], the bands at 1,445, 1,590 and 1,623 cm^{-1}

**Fig. 2. FT-IR spectra of n-butylamine adsorbed on Na-bentonite and modified samples.**

are mainly assigned to a Lewis acid site. This may arise from terminal Al ions in the clay [24]. The peak at 1,540 is assigned to Brönsted acid site. This may arise from the hydroxyl groups attached to Zr [25] and the structural hydroxyl groups attached to Al/Mg in the PILC [25,26]. However, according to [27] aluminol and magnesol groups do not possess strong Brönsted acid character. Therefore, it may be inferred that the strong Brönsted acidity observed in the present study is due to hydroxyl groups in hydrated zirconia as suggested by [28]. The band at $1,490\text{ cm}^{-1}$ is attributed to both Lewis and Brönsted acid sites. At 298 K, all of the PILC contained enormously high surface acidity compared to the original bentonite. This simply indicates that the acidity of the clay is enhanced by pillaring the clay. On thermal treatment at 473 K, the band at $1,445\text{ cm}^{-1}$ in the spectrum of $\text{Zr}_{\text{DR}}\text{-G}$ and $\text{Zr}_\text{I}\text{-G}$ disappeared, showing that at this temperature the Lewis sites present are not strong enough to interact with *n*-butylamine. Whereas, slight reduction in the intensity of the peaks (of both Brönsted and Lewis acidity) was observed in the case of the sample prepared with the direct method. The addition of the cerium has an important effect on the surface acidity of PILC. In fact, as shown in Fig. 2, the addition of the cerium leads to the appearance, in all samples, of a new IR band at $1,638\text{ cm}^{-1}$, stable until 873 K, corresponding to Brönsted acid sites [29]. Moreover, the bands assigned to *n*-butylamine coordinated onto Lewis acid sites ($1,445\text{ cm}^{-1}$) in the case of $\text{Ce-Zr}_{\text{DR}}\text{-G}$ and $\text{Ce-Zr}_\text{I}\text{-G}$ remain after evacuation at 673 K, which suggests the stronger nature of the Lewis acid sites when compared to the $\text{Zr}_{\text{DR}}\text{-G}$ and $\text{Zr}_\text{I}\text{-G}$ samples. This result indicates that cerium improves the Lewis and Brönsted acidity on the surface. Finally, the intensities of the bands assigned to *n*-butylamine coordinated onto Lewis and Brönsted acid sites are slightly reduced in all samples after thermal treatment.

2. Activity of the Pillared Clays in CWPO of Phenol

According to the reaction pathway carried out by [30], phenol conversion leads to aromatic intermediates like hydroquinone and benzoquinone. And the aromatic intermediates evolve to carboxylic acids. Here, we study only the time-curve evolution of the phenol and the TOC conversion. The phenol conversion in function of the reaction time, for the three modified solids and the natural Na-G clay (Fig. 3), revealed that the starting natural clays, Na-G, used in this catalytic reaction are quite active. Calcined Na-G only reached 31% conversion of phenol after 4 h of reaction. The non-

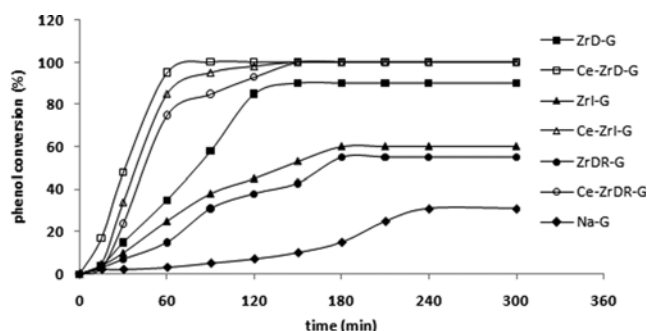


Fig. 3. Oxidation of phenol by H_2O_2 catalysed by Na-G, Zr- and Ce-Zr-pillared clay in diluted aqueous medium at atmospheric pressure and at 298 K.

negligible catalytic activity obtained for natural calcined clay can be explained by the initial content of iron oxides found in natural clay (8.03%). [7]. The three pillared clays ($\text{Zr}_\text{D}\text{-G}$, $\text{Zr}_\text{I}\text{-G}$, and $\text{Zr}_{\text{DR}}\text{-G}$) show conversion values of phenol much higher than those of natural calcined bentonite. However, it is important to mention that the pillaring method drastically affects the activity for phenol oxidation. The Zr-pillared clays using the classic method 'D' show a higher activity than the 'I' and 'DR' ones. The percentage of conversion of phenol for modified solids ranges between 55% and 90%, being higher for the $\text{Zr}_\text{D}\text{-G}$. With $\text{Zr}_\text{D}\text{-PILCs}$, almost complete phenol conversion (90%) is reached in 2.5 h, whereas the $\text{Zr}_\text{I}\text{-G}$, and $\text{Zr}_{\text{DR}}\text{-PILCs}$ leads to no more than 53% in the same time. $\text{Zr}_\text{I}\text{-G}$, and $\text{Zr}_{\text{DR}}\text{-PILCs}$ require 3 h to reach a plateau. In a previous work, Carriazo et al. [31] showed that the variation of activity among the various catalysts correlates with the surface area, which enhances access of the reacting species to and from the active sites. In our case, samples have comparable surface area (199.5 , 190.6 , and $187.1\text{ m}^2\text{ g}^{-1}$ for $\text{Zr}_\text{D}\text{-G}$, $\text{Zr}_{\text{DR}}\text{-G}$, and $\text{Zr}_\text{I}\text{-G}$, respectively) and the same microporosity ($0.6\text{ cm}^3\text{ g}^{-1}$). Nevertheless, the direct method gives samples having the highest catalytic 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.

So, the great difference found in the catalytic behavior of these three solids cannot be the resulting consequence of the generation of microporosity in the pillared clay. But it seems to correlate especially with the zirconium content and the type of the acid center. Herein, the reason for the higher activity of solid prepared by the direct method is its higher amount of zirconium and the strength of Brönsted and Lewis acidity acid center as compared to samples obtained with "DR" and "I" method.

Concerning samples modified with cerium, the results of the catalytic evaluation of pillared clays confirm the beneficial effect of the introduction of Ce species into solids in the conversion of phenol (Fig. 3). The three pillared clays ($\text{Ce-Zr}_\text{D}\text{-G}$, $\text{Ce-Zr}_{\text{DR}}\text{-G}$ and $\text{Ce-Zr}_\text{I}\text{-G}$) show conversion values of phenol much higher than those without cerium under the same condition. In fact, complete phenol conversion (100%) is reached after 90 min of reaction in the presence of $\text{Ce-Zr}_\text{D}\text{-G}$, and 140 min with $\text{Ce-Zr}_{\text{DR}}\text{-G}$ and $\text{Ce-Zr}_\text{I}\text{-G}$. Whereas, in the case of catalyst poor in cerium species, the phenol conversion reached its maximum only with $\text{Zr}_\text{D}\text{-G}$ catalyst.

To assess the stability of active phase of pillared clays, the leachate zirconium and cerium in the medium were performed (Table 2). The leachate zirconium in the medium, after 4 h of reaction, was $17\text{ }\mu\text{mol}$ for $\text{Zr}_\text{D}\text{-G}$ and $\text{Zr}_\text{I}\text{-G}$, thus demonstrating the stability of the active phase. In the case of $\text{Zr}_{\text{DR}}\text{-G}$, the leachate zirconium in the medium was $9.94\text{ }\mu\text{mol}$. This fact shows that the fraction of zirconium leached from the catalyst is not capable of transforming the phenol, and the homogeneous part of the reaction, is of minor importance [32]. The leachate cerium in the medium shown in Table 2, after 4 h of reaction, was less than $15\text{ }\mu\text{mol}$, indicating the stability of the active phase in all samples modified with cerium.

TOC conversion levels (Fig. 3) follow the same tendency as the one obtained in the phenol reaction, confirming the beneficial effect of conventional method and synergism between zirconium and

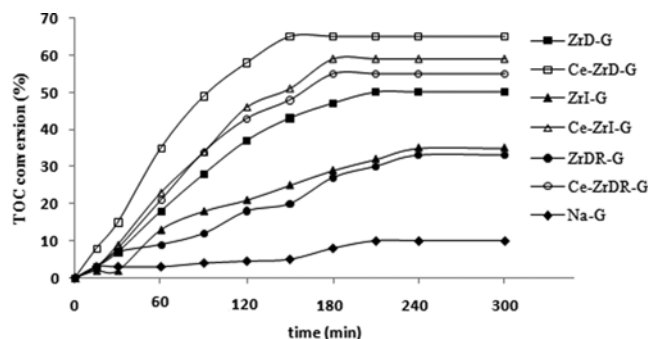


Fig. 4. Catalytic activity for different catalyst in the TOC conversion in diluted aqueous medium at atmospheric pressure and at 298 K.

cerium to reach values above 90%. Regarding the TOC conversion reaction (Fig. 4), the favorable effect of the Zr_D -G system can also be observed, which shows, as in the phenol reaction, better results than the Zr_{DR} -G and Zr_I -G system. Again, the cooperative effect between cerium and zirconium for TOC conversion is clear. After comparing the results with those obtained with Zr-modified clay, the enormous catalytic potential of these materials once they have been modified via pillaring with mixed Ce-Zr-systems is evident. As a matter of fact, TOC conversion is enhanced from 50% (after 210 min) to 65% (after 150 min) in the case of Zr_D -G and Ce- Zr_D -G, respectively. The same tendency is observed in the case of samples prepared with 'I' and 'DR' methods. In fact, Fig. 4 reveals that TOC conversion increases from about 35% (after 240 min) in the case of Zr_{DR} -G and Zr_I -G catalyst to 55% and 58% (after 180 min) in the case of Ce- Zr_{DR} -G and Ce- Zr_I -G catalyst, respectively.

CONCLUSIONS

We completed an investigation of Zr-PILCs and Ce-Zr-PILCs prepared with three methods. The study of the effect of cerium addition and the influence of the pillaring method on Zr-PILCs shows that:

(i) The pillaring method is a determining factor in the polymerization of zirconium: a successful pillaring process is obtained by the hydrolysis of the zirconium precursor using either the 'D' or the 'I' method. But, under reflux conditions, a delamination of the clay structure was observed.

(ii) The cerium incorporation constitutes a new way of synthesis that allows the conservation of structural and textural properties of the pillared clay, using refluxed method.

(iii) The catalytic tests confirm that pillared clays rich in cerium, in spite of the very low cerium content of the Ce-Zr pillared materials, show conversion values of phenol and TOC much higher than those without cerium under the same condition.

REFERENCES

1. C. Catrinescu, C. Teodosiu, M. Macoveanu, J. Miehe-Brendle and R. Le Dred, *Water Res.*, **37**, 1154 (2003).

2. D. E. W. Vaughan, R. J. Lussier and S. J. J. Magee, US Patent, 4,176,090 (1979).
3. E. Booi, T. J. Klopogge and J. A. Rob van Veen, *Appl. Clay Sci.*, **11**, 155 (1996).
4. A. Gil, M. Gandia and M. A. Vicente, *Catal. Rev. Sci. Eng.*, **42**, 145 (2000).
5. L. Huerta, A. Meyer and E. Choren, *Micropor. Mesopor. Mater.*, **57**, 219 (2003).
6. S. B. Chaabene, L. Bergaoui and A. Ghorbel, *Appl. Catal. A: Gen.*, **268**, 25 (2004).
7. J. Carriazo, E. Guelou, J. Barrault, J. M. Tatibouet, R. Molina and S. Moreno, *Water Res.*, **39**, 3891 (2005).
8. J. Carriazo, E. Guelou, J. Barrault, R. Molina and S. Moreno, *Catal. Today*, **107-108**, 126 (2005).
9. M. J. Hernando, C. Pesquera, C. Blanco and F. Gonzalez, *Chem. Mater.*, **13**, 2154 (2001).
10. S. K. Kim and S. K. Ihm, *Ind. Eng. Chem. Res.*, **41**, 1967 (2002).
11. S. Mnasri, N. Besbes, N. Frini-Srasra and E. Srasra, *C. R. Chem.*, **15**, 437 (2012).
12. S. Mnasri and N. Frini-Srasra, *Clay Miner.*, **47**, 453 (2012).
13. S. Mnasri and N. Frini-Srasra, *Inf. Phys. Technol.*, **58**, 15 (2013).
14. S. Mnasri and N. Frini-Srasra, *Surf. Eng. Appl. Electrochem.*, **49**, 336 (2013).
15. E. M. Farfan, E. Sham and P. Grange, *Catal. Today*, **15**, 515 (1992).
16. R. Toranzo, M. A. Vicente, M. A. Banares-Munoz, L. M. Gandia and A. Gil, *Micropor. Mesopor. Mater.*, **173**, 173 (1998).
17. J. Poyato, M. M. Tobias and J. M. Trillo, *Inorg. Chim. Acta*, **14**, 307 (1987).
18. M. L. Occelli, *Catal. Today*, **2**, 339 (1988).
19. S. Zuo, Q. Huang, J. Li and R. Zhou, *Appl. Catal. B: Environ.*, **91**, 204 (2009).
20. N. R. Sanabria, M. A. Centeno, R. Molina and S. Moren, *Appl. Catal. A: Gen.*, **356**, 243 (2009).
21. M. Chen, L. Fan, L. Qi, X. Luo, R. Zhou and X. Zheng, *Catal. Commun.*, **10**, 838 (2009).
22. Q. Huang, S. Zuo and R. Zhou, *Catal. Commun.*, **95**, 327 (2010).
23. Y. G. Yin, *Research methods of heterogeneous catalysts, chemical industry*, Press, Beijing, 582 (1988).
24. S. V. Awate, S. B. Waghmode and M. S. Agashe, *Catal. Commun.*, **5**, 407 (2004).
25. J. Lambert and G. Poncelet, *Top. Catal.*, **4**, 43 (1997).
26. T. J. Pinnavaia, M. Tzou and S. D. Landau, *J. Am. Chem. Soc.*, **107**, 4783 (1985).
27. P. Cool and E. F. Vansant, *Mol. Sieves*, **1**, 265 (1998).
28. E. M. Farfan-Torres, E. Sham and P. Grange, *Catal. Today*, **15**, 515 (1992).
29. H. J. Chae, I. S. Nam, S. W. Ham and S. B. Hong, *Catal. Today*, **68**, 31 (2001).
30. H. Devlin and I. Harris, *Ind. Eng. Chem. Fund.*, **23**, 387 (1984).
31. J. G. Carriazo, R. Molina and S. Moreno, *Appl. Catal. A: Gen.*, **334**, 168 (2008).
32. J. Barrault, M. Tatibouet and N. Papayannakos, *Comptes Rendus de l'Academie des Sciences - Series IIC - Chemistry*, **3**, 777 (2000).