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The effect of ultrasound in the synthesis of clays used as catalysts in oxidation reactions

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Abstract

The effect of ultrasound in the modification of a Colombian bentonite pillared with mixed solutions of Al–Ce and Al–Ce–Fe was obtained. The solids were characterized by means of X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques. The catalysts were very efficient in the phenol oxidation reaction in diluted aqueous medium under mild experimental conditions (298 K and atmospheric pressure) and in the CO oxidation reaction. The use of ultrasound showed a clear effect in the synthesis of this type of solids allowing to make their synthesis in a shorter period of time and conserving the physical–chemical characteristics as well as catalytic activity in the oxidation reactions.

Keywords: Pillared clays; CWPO reaction; Ultrasound; Phenol oxidation

1. Introduction

The presence of toxic organic compounds in wastewaters issued from industry has challenged conventional treatment methods, encouraging the development of new purification techniques in the past decade.

Advanced oxidation processes for the treatment of non-biodegradable toxic organic pollutants contained in industrial effluents, including phenol, provide a good alternative to already existing techniques such as incineration, flocculation, precipitation, adsorption, reverse osmosis and/or chemical treatments [1,2].

Among advanced oxidation processes, the activation of hydrogen peroxide by means of a solid catalyst (catalytic wet peroxide oxidation CWPO), is the most promising process, both economically and technologically [3].

Catalytic oxidation of CO has been the object of several studies in the past few years, revealing the catalytic activity of precious metals (Pt, Pd, and Au) supported on clay-like material.

Pillared clays have offered an important line of research in obtaining solids responding to the CWPO process. In fact, since the first report on this type of materials was made by the end of the 1970s [5], a considerable number of studies have been carried out in order 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. A solution proposed to this problem is the addition of a second metal to the pillaring solution [6–11].

Extensive work in this field points to the synthesis of mixed pillars with applications in environmental processes [6,8,12–15]. Some works on the synthesis of pillared clays with mixed species have shown that the use of transition metals allow the production of solids with a high oxidation power. The incorporation of iron in aluminium pillars reveals a system which is competent in the oxidation of organic matter. However, the low stability characterizing by the active phase (Fe) turns it into yet another pollutant. One of the options that have been tested to solve this inconvenience and to improve the

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catalytic properties of this metal phase was the addition of another cation to improve the stability, activity and selectivity of the Al–Fe mixed system [16–18]. The incorporation of cerium into these systems favours the dispersion of the active phase and enhances the redox properties of the material.

One of the essential parameters in the preparation of pillared clays is the time and mode of aging both for pillaring solutions and during the intercalation process. A reduction of time at these stages would significantly favour the possible increase in the preparation of these solids at industrial level. In the past few years, several techniques have been tested to facilitate and increase the incorporation of polyhydroxications within the structures of these solids, including reflux, microwaves and ultrasound among others. The latter has made it possible to obtain interesting results in the modification of clays via pillaring with aluminium [19–22].

Singh et al. [21] report on a method for preparing modified clays with ZrO_2 using ultrasound in the intercalation process, finding an increase in the surface area and a thermally stable interlaminar spacing due to a better distribution of ZrO_2 species in the clay.

Katdare et al. [19,21] have discussed the benefits of using ultrasound in the modification of clays via aluminium pillaring and have revealed a significant thermal stability in these solids (temperatures higher than 800 °C) and a considerable reduction in the contact times between the clay and the pillaring solution in the intercalation stage.

Within this context, this paper describes the synthesis of a modified Colombian bentonite by pillaring with mixed solutions of Al–Ce and Al–Ce–Fe and the effect of ultrasound, employed for the first time in the preparation of mixed solutions (three metals), as an essential step in the preparation of these solids.

2. Experimental

The clay is a bentonite issued from Valle del Cauca, Colombia. In order to approach the clay to a homoionic form and to facilitate the exchange process with the polyhydroxication, this was homoionized with a sodium chloride solution.

The modification via pillaring with the Al–Ce species is carried out by adding a solution of chlorhydrol (ACH) 0.1 M to a solution of cerium, keeping a Ce/(Ce + Al) atomic ratio of 0.1. The solution is aged by constant stirring at room temperature for 24 h. Additionally, an Al–Ce solution is prepared and aged for 10 min under the effect of ultrasound.

The Al–Ce–Fe species were prepared forming first an Al–Fe solution, using ferric nitrate and the ACH, with a Fe/(Fe + Al) atomic ratio of 0.1 and an OH^-/M molar ratio of 2.5. The solution is aged under continuous stirring at room temperature for 24 h and then, the necessary amount of $Ce(NO_3)_3{\cdot}6H_2O$ is added to reach an atomic ratio of 0.2 Ce/(Fe + Al + Ce). The solution obtained is aged by means of two different methods: (1) at room temperature for 24 h (24) and (2) through the intervention of ultrasound for 10 min (US).

The pillaring solutions are slowly added to a suspension of clay (2%, w/w) under vigorous stirring. The temperature during the exchange is 18 °C. The final clay suspension is later on aged through two different methods; at room temperature for 24 h, and 10 min under the effect of ultrasound, keeping a frequency of 50 kHz. Finally, the solids are washed by centrifugation, dried at 60 °C for 12 h, and then calcinated at 400 °C for 2 h.

The solids are designated according to their synthesis variable: AlCe24US, AlCeUS24, AlCeFe24US, AlCeFeUS24 and AlCeFe2424, where AlCe24US corresponds to the clay modified with AlCe whose modifying solution is aged at 24 h and the exchange is carried out by 10 min in ultrasound.

2.1. Characterization

The chemical analysis of the starting material and of the Al–Ce–Fe modified samples was determined by X-ray fluorescence (Philips MagiX Pro PW2440, samples prepared in pearls).

The X-ray diffraction (XRD) study was done in a Philips device, which operates with Cu Kα radiation.

2.2. Catalytic activity

The catalytic oxidation reaction of phenol in a diluted aqueous medium was carried out in a semi batch glass reactor (pyrex) with a capacity of 250 ml, open to the atmosphere, thermostated at 298 K, 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 (0.1 M) was added at a 2 mL/h flow and during a reaction time of 4 h. The pH was continuously adjusted to 3.7 and an air flow was introduced in the reactor at a ratio of 2 L/h. 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 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-190 device.

CO oxidation reaction was performed in a U-shaped glass reactor working at atmospheric pressure. The light-off curves of CO oxidation (from room temperature to 400 °C at 5 °C/min) were obtained by having a flow of 42 ml/min of a mixture of 3.4% CO, 21% O_2 and 75.6% He (prepared with mass flow controllers) pass over 80 mg of sample placed among quartz wools. The reaction was followed by a mass spectrometry, using a Balzers Thermostar benchtop mass spectrometer controlled by the software Balzers Quadstar 422 with capabilities for quantitative analysis. Empty reactor shows no activity under such conditions. Prior to the reaction, catalysts were activated in situ for 1 h at 400 °C with 30 ml/min of a mixture of 21% O_2 in He and the stabilized at room temperature before the light-off curve started.

Table 1
Characterization of the solids: chemical analysis and DRX

Solid	Fe_2O_3 (%)	Al_2O_3 (%)	CeO_2 (%)	d_{001} (Å)
Natural clay	6.03	9.83	–	15.0
AlCeUS24	8.00	23.32	0.37	17.7
AlCe24US	7.50	24.20	0.25	17.2
AlCeFeUS24	10.91	22.14	0.09	16.7
AlCeFe24US	9.31	22.10	0.16	17.7
AlCeFe2424	10.71	20.04	0.14	17.0

3. Results and discussion

3.1. Characterization

Table 1 shows the results of the chemical analysis obtained by X-ray fluorescence and the value of the basal spacing (d_{001}) of modified solids obtained by DRX. The elementary analysis shows an increase in the amounts of iron and aluminium with respect to natural bentonite (B-natural), showing an effective introduction of these metals in the starting material. Likewise, the introduction of cerium in the samples is revealed, showing a practically constant value (0.1%) in solids modified with the mixed system Al–Ce–Fe, while materials modified only with Al–Ce show greater values, which could be associated to a competitive phenomenon between iron and cerium during the intercalation process.

The DRX results show that, in all solids, the modification of the clays carried out via pillaring is successful (shifting of d_{001} to higher values, Fig. 1 and Table 1). It was observed that the use of ultrasound during the process of aging of Al–Ce pillaring solution leads to a solid with a greater spacing (∼18 Å) than that observed for the one obtained when applying the US during the intercalation of clay (∼17 Å). The above confirms a beneficial effect of the US in the process of aging during clay modification, as reported by Katdare et al. [19,21].

It is important to highlight that the ultrasound treatment considerably reduces the needed modification time for solids, since in just 10 min we get very similar results to those obtained with prolonged synthesis times (24 h (Al–Ce–Fe2424)).

3.2. Catalytic activity

Solids modified via pillarization of the Colombian bentonite with Al–Ce or Al–Ce–Fe possesses excellent catalytic properties

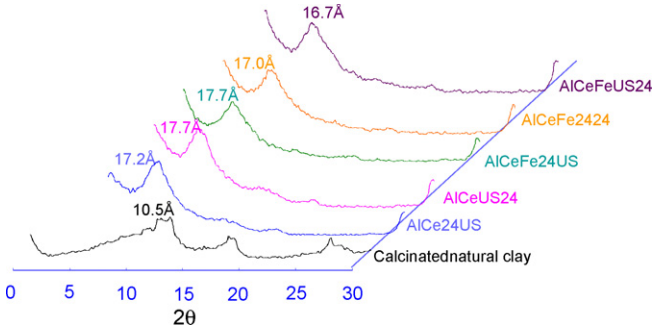

Fig. 1. X-ray diffraction patterns of the natural clay and of the modified solids.

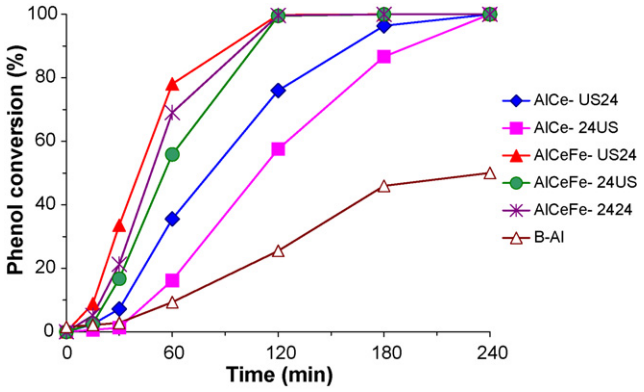

Fig. 2. Catalytic activity of the modified clays in phenol oxidation reaction.

in the phenol oxidation reaction. Likewise, considerable activity is found in the CO reaction (Figs. 2–4 and Table 2), whose activity could be improved if a precious metal is incorporated [4,23]. A synergic behaviour between Fe and Ce in the oxidation reaction can be identified from the results obtained. In fact, in the two reactions assessed, the solids modified with the mixed species Al–Ce–Fe show better results than the solids modified with Al–Ce species.

In Fig. 2, which shows the phenol conversion in function of the reaction time for the five modified solids and the natural clay modified with aluminium (B–Al), we can observe that all solids reach 100% phenol conversion, and in some cases, this is achieved within the first 2 h of the reaction. The conversion obtained with the clay modified only with aluminium is the product of the activity characterizing by the iron species found in the octahedral layers of these materials, as established in previous works [17,18]. As already mentioned, it has been found that clays modified with mixed pillar Al–Ce–Fe show better phenol conversion than those modified only with Al–Ce.

COT conversion levels (Fig. 3) follow the same tendency than the one obtained in the phenol reaction, confirming the beneficial effect of ultrasound and synergism between iron and cerium to reach values above 50% (Table 2).

On the other hand, it is important to mention that the use of ultrasound as an aging way for the pillaring solution allow to have more active solids than those obtained when ultrasound is

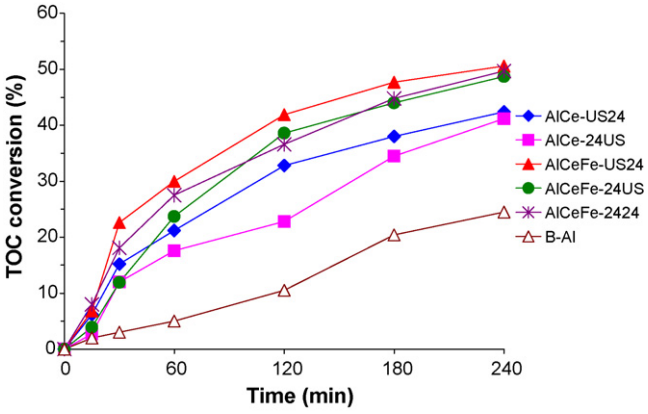

Fig. 3. TOC elimination by the modified clays in the phenol oxidation reaction.

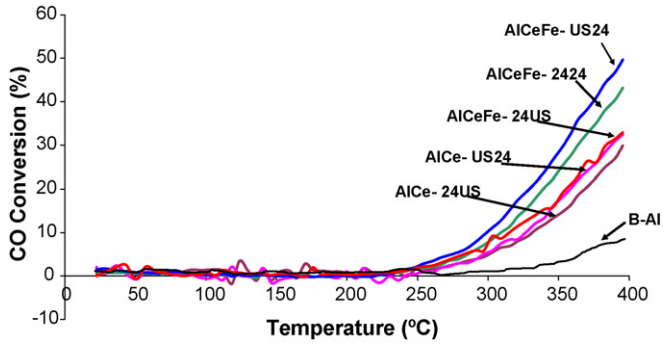

Fig. 4. Catalytic activity of the modified clays in CO oxidation reaction.

Table 2
Conversion of phenol and COT of the catalysts at 298 K, and atmospheric pressure during 4 h of reaction

Solid	Phenol conversion (%)	COT conversion (%)	CO conversion (%) 400 °C
B–Al	50	29	8
AlCeUS24	100	42	32
AlCe24US	100	41	30
AlCeFeUS24	100	51	50
AlCeFe24US	100	49	33
AlCeFe2424	100	50	43

applied in the intercalation process. This effect is found in the two systems assessed (Al–Ce–Fe and Al–Ce) and can be attributed to the probable effect of ultrasound on the clay, causing a loss in the textural characteristics of the solid. It is worth pointing out that the results of catalyst Al–Ce–FeUS24 are comparable and surpass those obtained for the modified clay through the traditional method (Al–Ce–Fe2424).

Regarding the oxidation reaction for carbon monoxide (Fig. 3), the favourable effect of the Al–Ce–Fe system can also be observed, which shows, as in the phenol reaction, better results than the Al–Ce system. Again, the cooperative effect between cerium and iron for oxidation reactions is clear. After comparing the results with those obtained with Al-modified clay, the enormous catalytic potential of these materials once they have been modified via pillaring with mixed Al–Ce–Fe systems is evident, since the conversion of clay modified only with Al reaches only 8%, as compared with 51% at 400 °C for the solid Al–Ce–FeUS24. The effect of ultrasound is reasserted as an efficient method in the preparation of these solids, reducing time considerably, going from 24 h for aging a pillaring solution to just 10 min, a reduction that can result in a critical factor in a possible scaling in the synthesis of these materials.

4. Conclusions

The use of ultrasound during aging, allows the modification of a bentonite via pillaring with mixed systems Al–Ce–Fe. The solids synthesized through this method are catalytically active in two environmental impact reactions, the phenol oxidation reaction and the carbon monoxide oxidation.

The addition of Fe and Ce in the aluminium pillar results in much more active materials.

The ultrasound employed during the aging process for the pillaring solution is more efficient than the one used during the aging in the intercalation.

The ultrasound considerably reduces the modification time for solids, since in just 10 min we get very similar results to those obtained with prolonged synthesis method (24 h).

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