# Activity and resistance of iron-containing amorphous, zeolitic and mesostructured materials for wet peroxide oxidation of phenol

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**Abstract**

Iron containing materials have been prepared following several strategies of synthesis and using different silica supports (amorphous, zeolitic and mesostructured materials). Activity and stability of these materials was evaluated on heterogeneous Fenton-type processes for the removal of phenol under mild reaction conditions (T=100º, P=0.1 MPa). Their catalytic performance was monitored in terms of phenol and total organic carbon (TOC) conversions, by-products distribution (aromatics compounds and carboxylic acids) and degree of metal leached into the aqueous solution. The nature and local environment of iron species is strongly dependent on the synthetic route, which dramatically influences on their catalytic performance. Crystalline iron oxide species supported over mesostructured SBA-15 materials have demonstrated to be the most interesting catalysts for phenol degradation according to its high organic mineralization, low sensitive to be leached out and better oxidant efficiency for Fenton like reactions.

# 1. INTRODUCTION

Over the past two decades, the growing concern about the removal of pollutants from wastewater streams have led and stimulated the development of treatment technologies to contend with tightening regulations. Fenton homogeneous reactions based on dissolved iron ions in presence of hydrogen peroxide [1-3] have been widely used for the oxidation of wastewater streams with medium-high TOC content (typically higher than 500 ppm). However, the limited range of the pH (3-5) in which the reaction proceeds and the need of recovery of the homogeneous catalyst are the major drawbacks of the Fenton process. In this sense several attempts have been described in the literature for the immobilization of iron species over different supports, searching for active and hydrothermally stable materials in a wide pH range.

Iron-containing zeolites have evidenced a remarkable catalytic activity in presence of $H_2O_2$ under acidic solutions for the removal of phenol [4-5] and other refractory organic compounds [6-7]. Pillared clays have been also modified with iron species and used for the treatment of phenolic aqueous solutions [8-10]. However, the extension to other materials such as mesostructured materials or metallic oxides needs to be explored for application in catalytic oxidation processes. In this sense, Crowther and Larachi [11] have recently reported the catalytic performance of different iron containing MCM-41 and HMS mesostructured materials for catalytic wet peroxide oxidation (CWPO) of phenol. The results show a significant dependence of the synthetic route used for their preparation on the activity and stability of the catalysts.

The main aim of this contribution is to evaluate and compare the activity and stability of iron species incorporated in distinctive ways over different silica structures in the CWPO of phenol. Crystalline iron oxides supported over amorphous silica and mesostructured SBA-15 material have been synthesised. Additionally, iron species have been incorporated by isomorphous substitution of silicon into the SBA-15 and MFI silicalite framework. Finally, an amorphous mixed $SiO_2$-$Fe_2O_3$ oxide synthesized by a sol-gel method has been also prepared. The catalytic performance of all above-mentioned materials has been monitored in terms of phenol and total organic carbon (TOC) conversions as well as efficient use of the oxidant. Likewise, a special interest has been focused on the resistance to leaching of active species and their relation with the local iron environment observed by means of spectroscopic techniques. Phenol has been used as a model reactant, because phenolic wastes are one of the most prevalent forms of chemical pollutants in industry today and characterised by a high toxicity and a poor biodegradability.

## 2. EXPERIMENTAL SECTION

### 2.1. Catalysts preparation

*Iron containing SBA-15 mesostructured materials* were prepared by co-condensation of iron ($FeCl_3 \cdot 6H_2O$; Aldrich) and silica (tetraethoxysilicate, TEOS; Aldrich) sources under acidic conditions and templated with Pluronic 123 as described elsewhere [12]. The resultant solution was aged at 110 ºC for 24 h under static conditions (S-1 sample). The procedure was slightly modified changing the ageing pH to 3.5 (S-2 sample) and 7 (S-3 sample) by addition of appropriate amount of ammonia aqueous solutions with the purpose of increasing the incorporation of iron species. After ageing step, the solid product was recovered by filtration

and air dried at room temperature overnight. The template was removed by calcination in air at 550ºC for 5 hours.

*Amorphous SiO$_2$-Fe$_2$O$_3$ mixed oxide* was prepared by two step sol-gel process developed by Uguina *et al*. [13], based on acid-catalyzed hydrolysis of the respective precursors (FeCl$_3$·6H$_2$O and TEOS) and followed by basic condensation with tetrapropylammonium hydroxide (TPAOH; Alfa). Solid was prepared with initial SiO$_2$/Fe$_2$O$_3$ molar ratio of 155 and denoted as S-4 sample.

*Iron containing zeolitic material* was synthesised through hydrothermal crystallisation of wetness impregnated amorphous SiO$_2$-Fe$_2$O$_3$ xerogels with aqueous 20 wt. % TPAOH solutions (S-**5** sample) [14]. The crystallization of the incipient wet impregnated solid was carried out in teflon-lined autoclaves under autogenous pressure and static conditions at 170 ºC. After this treatment, the solid products of the synthesis were separated by centrifugation, washed several times with distilled water and dried overnight at 110 ºC. The calcination of the samples was carried out in air at 550 ºC for 7 hours.

## 2.2. Catalysts characterisation

Characterisation of the samples was performed by different conventional techniques. X-ray powder diffraction data were acquired on a Philips X-Pert diffractometer using Cu K$\alpha$ radiation. The data were collected from 2$\theta$ ranging from 0.5 to 90º with a resolution of 0.02º. Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics Tristar 3000 System. Diffuse reflectance UV-VIS spectra (DR UV-VIS) were obtained under ambient conditions on a Varian Cary-500 spectrophotometer equipped with a diffuse reflectance accessory in the wavelength range of 200-600 nm. Transmission electron

microscopy (TEM) microphotographs were carried out on a PHILIPS TECNAI-20 electron microscope operating at 200 kV. Iron content of the synthesised samples was performed by means of Atomic Emission Spectroscopy with Induced Coupled Plasma (ICP-AES) analysis collected in a Varian Vista AX system.

## 2.3. Catalytic experiments

Catalytic wet oxidation experiments in presence of hydrogen peroxide were carried out in a 100 mL glass autoclave reactor under continuous mechanical stirring (350 rpm) in contact with air. The appropriate amount of catalyst suspended in water (0.6 g/L) was placed into the glass reactor. Thereafter, the system was pressurised with air and heated up to 100ºC. Once the temperature reached 100ºC, the required amount of $H_2O_2$ and phenol (5.1 and 1.0 g/L, respectively) were added. Then, aliquots were withdrawn during the reaction course with the purpose of monitoring the evolution of phenol and TOC removal, hydrogen peroxide conversion and intermediate products distribution. HPLC chromatograph model Varian Prostar equipped with a Waters Spherisorb column and an UV detector was used for the determination of phenol and hydrogen peroxide conversions as well as quantitative analysis of by-products coming from incomplete mineralization of phenol. Total organic carbon (TOC) content of the solutions before and after reaction was analysed using a combustion/non dispersive infrared gas analyser model TOC-V Shimadzu. Iron content in the filtered solution after reaction was measured by ICP-AES analysis collected in a Varian VISTA AX system.

## 3. RESULTS AND DISCUSSION

3.1 *Catalyst properties*

Table 1 lists the main physicochemical and textural properties as well as the iron content of the calcined samples after synthesis. XRD spectra of the samples, depicted in Figure 1 and summarised in Table 1, reveal the different structural order and the presence of crystalline phases of the synthesised materials. It can be easily inferred that the increase of pH during ageing of iron-containing SBA-15 materials promotes the appearance of crystalline oxide entities (mainly as hematite) with a gradual disappearance of mesoscopic order and decreasing of the specific surface area (samples S-1, S-2 and S-3). Note that S-3 sample evidences a complete absence of mesoscopic order and a low surface area. The presence of the hematite particles detected by XRD spectra for samples S-2 and S-3 have been also confirmed by TEM micrographs exhibiting a wide distribution of particle size ranging from 30 to 300 nm (see Figure 2). TEM images also prove the absence of hematite for S-1 sample as well as the presence of well ordered channels typical of 2D hexagonal symmetry of SBA-15 materials. Microanalysis measurements confirm the homogeneity of Fe content in the highly mesostructured material (S-1 sample), being in a good agreement with the bulk content determined by ICP-AES analysis. In contrast S-2 and S-3 samples show zones with a high concentration of Fe which are related with the micro-aggregates of hematite and low contents (ca. 3.6 % ) for the mesostructured zone.

Finally, XRD patterns also reveal the complete transformation of wetness-impregnated iron containing amorphous materials (S-4 sample) into a highly crystalline MFI zeolitic structure after the hydrothermal treatment (S-5 sample).

**Table 1.** Physicochemical properties of different Fe containing materials after synthesis

| Samples | Type of material | XRD | | Fe content | $S_{BET}$ | $D_p{}^a$ |
| | | Low Angle Order | High Angle Order | (% wt) | (m$^2$/g) | (Å) |
| --- | --- | --- | --- | --- | --- | --- |
| S-1 | Fe-SBA-15 | Yes | No | 1.2 | 715 | 86 |
| S-2 | Crystalline Oxide/SBA-15 | Yes | Yes | 16.0 | 468 | 68 |
| S-3 | Crystalline Oxide/SiO$_2$ | No | Yes | 22.0 | 295 | -$^b$ |
| S-4 | Amorphous | No | No | 1.2 | 872 | 30 |
| S-5 | Fe-Silicalite | No | Yes | 1.2 | 423 | 5.5 |

$^a$ Mean pore size. $^b$ Broad pore size distribution.
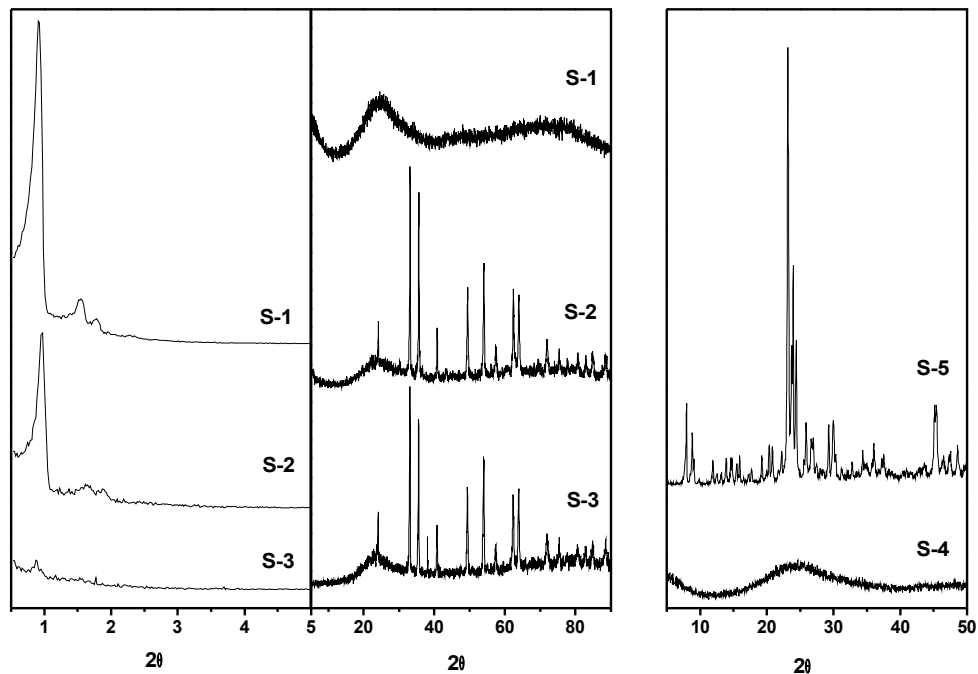


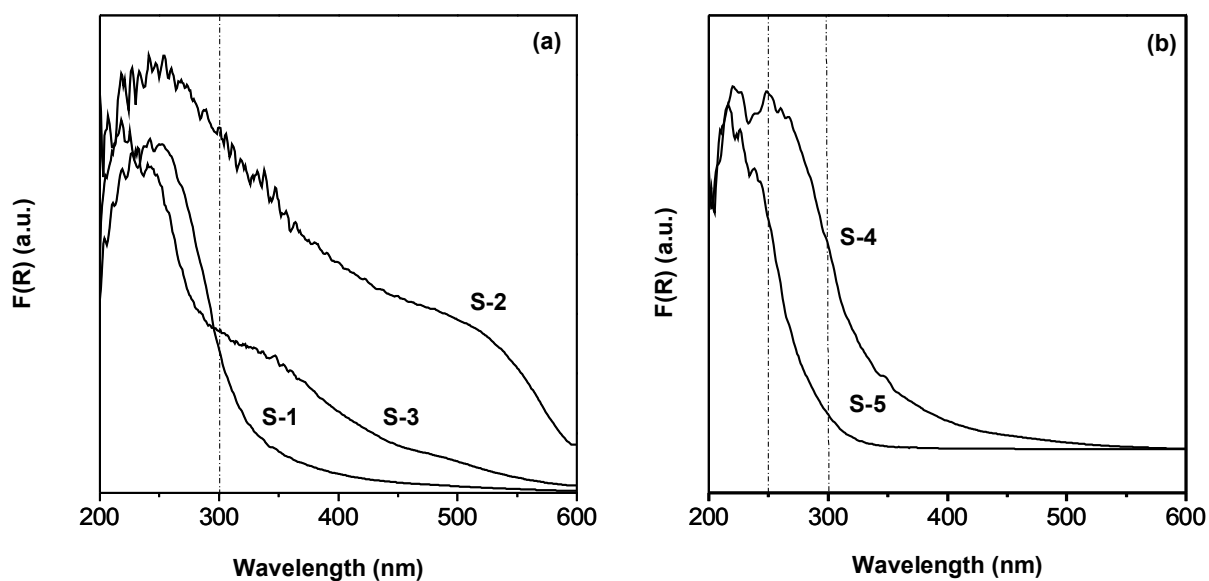**Figure 1**. XRD spectra of iron-containing materials.
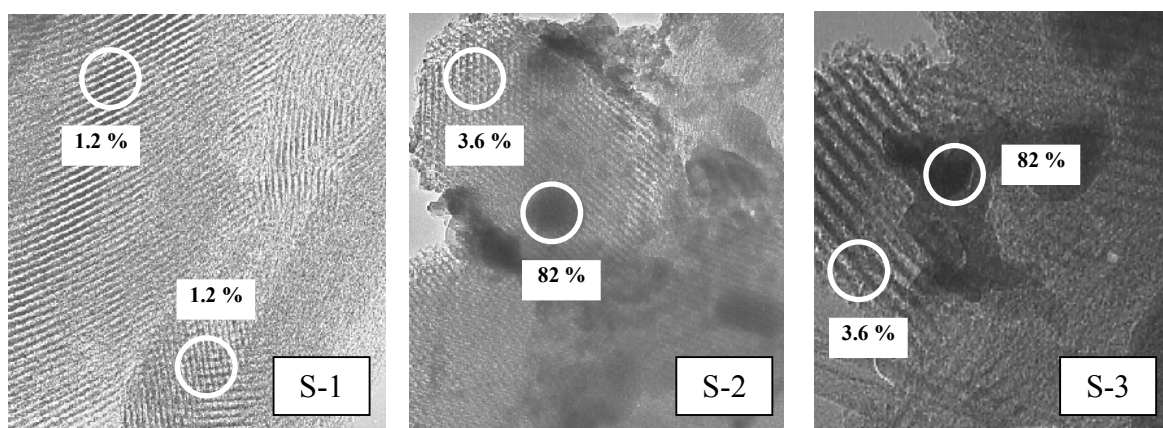
**Figure 2**. TEM images of S-1, S-2 and S-3 samples. Numbers indicate the percentage of iron in wt % measured by EDX microanalysis

In previous works the analysis of local iron environment in these materials has been deeply studied by means of Mössbauer experiments [14-15]. In strong acidic media (pH < 1; sample 1), iron is incorporated into the SBA-15 structure predominantly in ionic dispersion (with negligible amounts of Fe-O-Fe neighbours). Fe-SBA-15 samples aged in moderately acidic conditions (pH ~3.5) or neutral media are composite materials – they contain hematite particles embedded into the mesostructured matrix in a wide distribution of size (30 – 300 nm). At neutral pH mostly regular hematite is formed, whereas ageing in mild acidic media leads more disordered iron oxide phases [15]. At the same time, a small part of iron is present in ionic dispersion in the siliceous matrix being almost negligible for S-3 sample. Amorphous $SiO_2$-$Fe_2O_3$ xerogels is mainly constituted of $(Si-O-)_n Fe(OH)_{(4-n)}$ units resulting from the sol-gel process used for the preparation of this material [16]. In situ Mössbauer spectra recorded after evacuation (at 643 K) and reducing treatments (in CO at 623 K) reveal that this material is mainly constituted of "partially crystalline" species coming from calcination and dehydration of these units [14]. Finally, analogous spectroscopic Mössbauer analysis

demonstrated that iron species in Fe-silicalite are in framework positions isomorphously substituted within the MFI structure [14].

DR UV-Vis spectroscopy is a very useful technique for studying the electronic state of isolated transition metal ions. Figure 3.a illustrates the DR UV-VIS spectra of the different iron-containing mesostructured materials after calcination (S-1 to S-3 samples). S-1 sample shows a narrow absorption band in comparison to that of S-2 and S-3 samples. Absorption bands over 300 nm are attributed to small clusters or microaggregates of $Fe_2O_3$ particles [17]. These bands are clearly evidenced for S-2 and S-3 samples and negligible for S-1 sample. Amorphous xerogel (Figure 3.b) presents a strong absorption in the 200-333 nm interval (two peaks are clearly distinguished), suggesting a ligand to metal $Fe^{+3}$ charge transfer associated to isolated framework $Fe^{+3}$ species [17]. Likewise, it should be noted that $Fe^{+3}$ species in octahedral complexes over amorphous supports ($Al_2O_3$) have been also characterized by a strong CT absorption band about 277 nm. In zeolitic material, DR UV-VIS absorption band shifts towards lower wavelengths and the band located at 250 nm almost disappears. This fact may be attributed to the gradual incorporation of tetrahedral iron atoms within the zeolitic framework from the different $Fe^{+3}$ species located in the xerogel as stated previously in Mössbauer spectroscopic results. DR UV-Vis spectroscopic results are in agreement with those obtained by Mössbauer spectroscopy and confirm without doubt the different local iron environments present in the synthesized samples.

**Figure 3**. DR-UV-VIS spectra of iron-containing synthesized materials.

*3.2 Activity in the CWPO of phenolic aqueous solutions*

It is well known that catalytic wet oxidation of phenol is a very complex process in which many types of intermediates as final products are involved. Several authors are outlined the main intermediates coming from partial oxidation of phenol [18-20]. These intermediate products include dihydric phenols, benzoquinones, carboxylic acids and other oxygenated compounds such as aldehydes and ketones. Figure 4 illustrates the activity of different iron containing materials after 10 and 90 minutes of reaction in terms of residual TOC concentration (expressed as percentage of remaining TOC) and the contribution of aromatic compounds (phenol, hydroquinone and cathecol), carboxylic acids (oxalic, acetic and formic acids) and other oxygenated compounds (other carboxylic acids, aldehydes and ketones). Catalytic experiments were performed with an initial peroxide concentration of 5.1 g/L,

corresponding to the stoichiometric amount for complete mineralization of phenol, according to the reaction:

$$C_6H_5OH + 14\ H_2O_2 \rightarrow 6\ CO_2 + 17\ H_2O$$
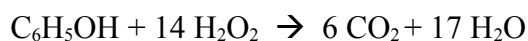
Note that all the catalytic systems yield better activity than the blank test carried out in absence of catalyst and with a stoichiometric amount of oxidant. Remarkable variations of activity are observed at 10 minutes of reaction for the different catalysts whereas fewer differences are found after 90 minutes of reaction. After 10 minutes, all the catalysts except zeolite (S-5 samples) showed a complete removal of phenol. Likewise, iron silicalite sample still evidence an important TOC concentration with traces of aromatic compounds and a significant fraction of carboxylic acids after 90 minutes of reaction. Note that zeolitic material containing similar iron content than S-4 (precursor amorphous xerogel) and S-1 samples exhibit a lower decrease of TOC conversion. This fact can be attributed to intraparticle diffusion problems arising from the limited pore size of the zeolitic materials.

It must be pointed out the outstanding activity of S-2 sample based on crystalline iron oxides supported over mesostructured SBA-15 as compared to S-1 sample (mostly iron isolated within the silica matrix) and S-3 sample (based on iron crystalline oxide supported over amorphous silica). This material achieves a 70% of TOC removal and the complete degradation of aromatics compounds in just 10 minutes of reaction. The presence of the mesostructured SBA-15 phase seems to have an important influence on the accessibility of organic matter to the active sites. Likewise, the remarkable hydrothermal stability of SBA-15 materials as compared to MCM-41 and HMS type structures [21] **make them more attractive for this kind of oxidation processes in liquid phase**.
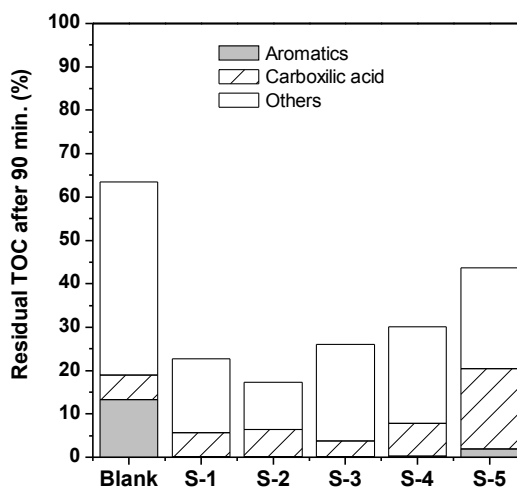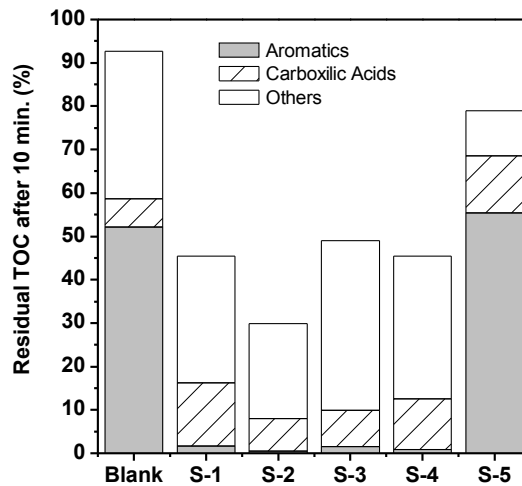
**Figure 4**. Activity of iron containing materials. Residual TOC after (a) 10 minutes and (b) 90 minutes.

A significant drawback of this kind of oxidation processes is the use of a relative high cost oxidant such as hydrogen peroxide. For this reason, one of the keys of Fenton processes is the efficient use of the oxidant that means a high TOC degradation with the lowest amount of oxidant as possible. Figure 5 displays the efficiency in the use of oxidant for the different catalysts, defined as TOC removal to hydrogen peroxide conversion ratio, after 10 and 90 minutes of reaction. Iron containing silicalite yielded low oxidant efficiency as compared with the rest of catalysts, especially for short reaction times. S-2 sample, consisting of crystalline

hematite supported over SBA-15 mesostructured silica, evidenced the best use of the oxidant in particular during the initial reaction times. It is well known that Fenton reactions are based on the **<u>hydroxyl</u>** radical**<u>s</u>** production by catalytic decomposition of hydrogen peroxide, which **<u>are</u>** responsible of a fast degradation and mineralization of the organic matter. However, hydrogen peroxide can also be decomposed to other inactive species through parallel reactions, which inhibit the oxidant power of hydrogen peroxide. From our catalytic results, the high catalytic performance achieved for S-2 sample is supported by their efficient use of oxidant after 10 minutes. This fact reveal that the nature of crystalline iron particles and the textural properties of the mesostructured silica matrix in which are supported (a surface area of ca. 470 m$^2$/g and a mean pore size of 68 Å) seem to be responsible of a more efficient use of the oxidant and higher TOC degradation. However, lower efficient of hydrogen peroxide is observed for S-3 sample with hematite crystalline entities immobilized in a non ordered amorphous silica matrix, S-1 sample with a well ordered SBA-15 mesostructure but with dispersed ionic iron species or S-4 sample with a high surface area but amorphous iron species.

Finally for longer reaction times a significant decrease of the efficient use of hydrogen peroxide for the mineralization of organic matter is clearly seen for all the catalyst, although in different extension. This fact must be attributed to the increase of refractory oxygenated by-products into the liquid phase as the reaction proceeds.
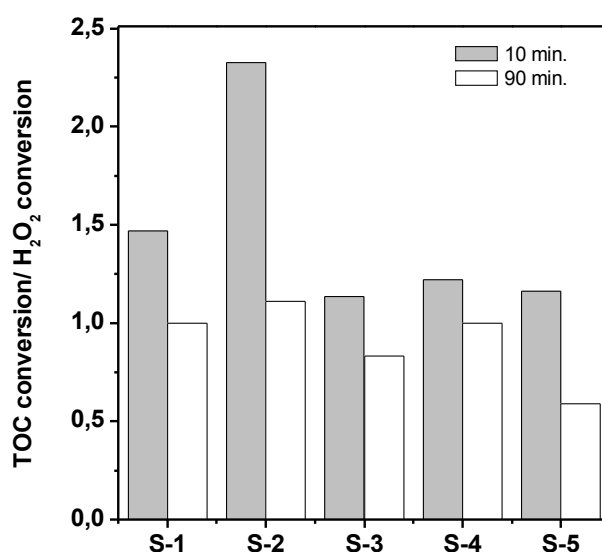
**Figure 5.** Efficiency on the use of oxidant after 10 and 90 minutes of reaction.

*3.3 Stability of catalysts in the CWPO of phenolic aqueous solutions*

A crucial point in the design of heterogeneous catalytic systems for WPO processes is the stability of metal species under the oxidant and acidic conditions in which the reaction occurs. Figure 6 shows the concentration of iron species into the aqueous solution after 90 minutes of reaction as well as the percentage of iron leached-off into the aqueous solution with respect to the initial amount of iron in the fresh catalyst. S-1 sample evidences a high leaching degree (ca. 75 % of the iron incorporated into the fresh catalysts) in comparison to those obtained for S-2 and S-3 samples (aged at higher pH) in which the presence of crystalline iron oxide species has been demonstrated by XRD and spectroscopic techniques. These crystalline oxide species are shown to be extremely resistant to be leached into the aqueous solution. Amorphous $Fe_2O_3$-$SiO_2$ mixed oxide (S-4 sample) has exhibited a significant loss of iron species after 90 minutes of reaction. Crystallisation of the amorphous $Fe_2O_3$-$SiO_2$ xerogels

(S-4 sample) into a zeolitic framework (S-5 sample) induces an enhancement of stability of active metal species. Note that in all the cases the Fe content within the aqueous solution is lower than 8 ppm.

The different local iron environments clearly observed in spectroscopic data results in distinctive metal stability. Crystalline iron oxide species are more resistant than ionic species isolated within mesostructured (S-1 sample) and amorphous (S-4 sample) supports. Low leaching evidenced for Fe-silicalite mighty be attributed to the high stability of iron species incorporated into MFI zeolitic framework.
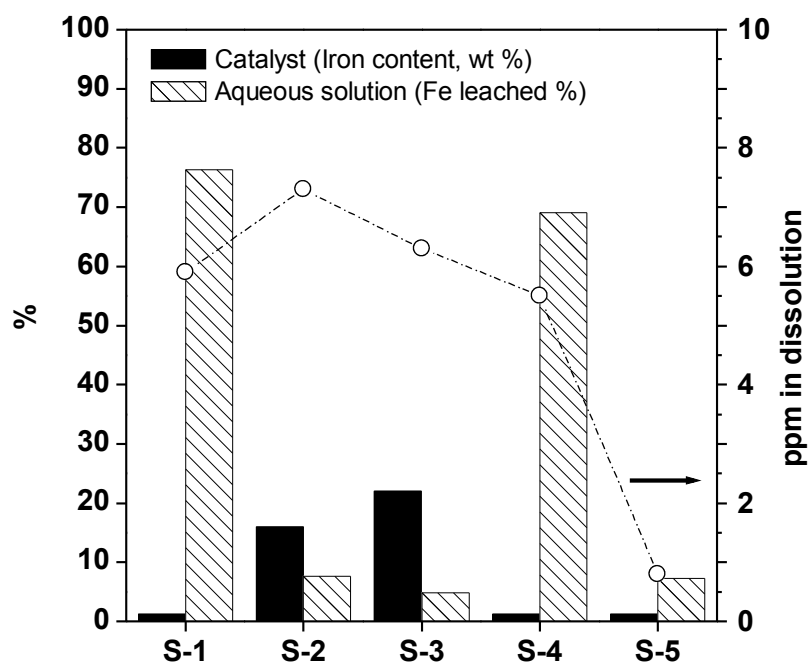


**Figure 6.** Stability of iron containing materials under WPO process.

*3.4 Homogeneous contribution of leached iron species in the oxidation reaction*

As the leaching of active species could play an important role on the CWPO of phenol further catalytic studies were carried out as follows. The resultant solution after 90 minutes of reaction using S-2 sample as catalyst was filtered in hot conditions to remove the catalyst.

Thereafter, phenol and hydrogen peroxide were further added to return then to the initial concentrations for running a new reaction. Figure 7 shows the TOC conversion of the filtered solution compared with the blank reaction and that carried out in presence of S-2 catalyst. The evolution of TOC conversion for filtered solution evidenced a lower initial activity in comparison to that shown by the heterogeneous system. After 10 minutes of reaction, TOC conversion of filtered solution was ca. 10 % whereas this value increased up to 70 % for the heterogeneous catalyst. Moreover, it must be noteworthy that the level of iron species dissolved into the aqueous solution at this initial stage is quite lower (less than 2 ppm) than that existing during the course of the filtered reaction (ca. 7 ppm). Note that after 90 minutes of reaction the TOC conversion for filtered catalytic run is higher than that obtained with the blank reaction but far from the heterogeneous system. These data demonstrate beyond doubt that the activity of the solid catalysts is not due just to a homogenous contribution of iron leached, but rather from the activity of heterogeneous catalyst.
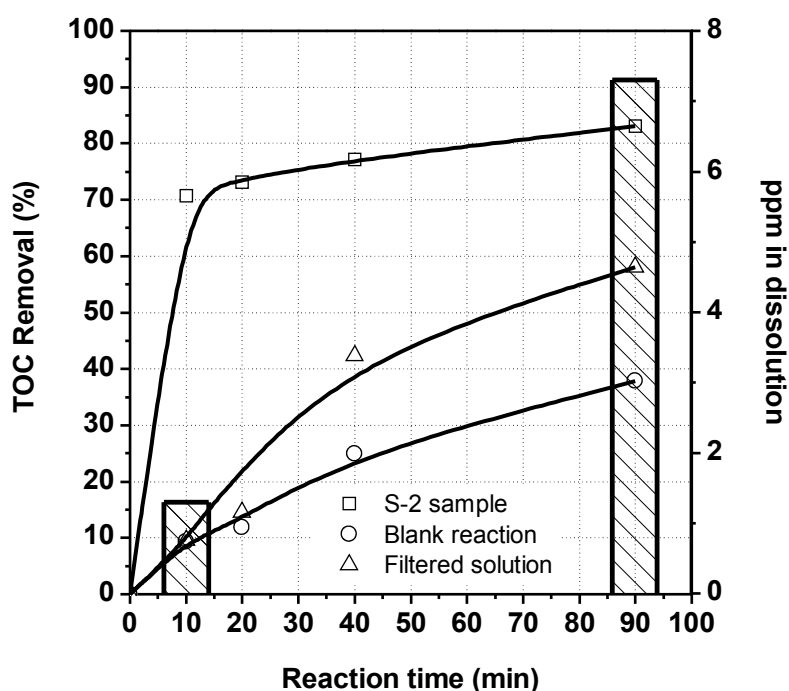


Figure 7. Contribution of homogeneous iron species in the WPO process. TOC conversion versus reaction time. Values of iron leached into the aqueous solution for S-2 sample are depicted in bar blocks at 10 and 90 minutes.

**4. Conclusions**

Activity and stability of iron containing catalysts for treatment of phenolic solutions by CWPO depend on the nature and environment of iron species, which is closely related with the strategy of synthesis. Iron crystalline oxides supported over mesostructured SBA-15 materials (S-2 sample) allow a complete removal of aromatic compounds with TOC reductions up to ca. 82% under mild reaction conditions. Likewise, an efficient use of the hydrogen peroxide and an outstanding low leaching of iron species (5%) accompany this catalytic performance. Therefore, this novel catalytic system joins all the desirable properties for being a promising catalyst for the oxidative degradation of organic pollutants and in particular for continuous industrial depollution processes. Nevertheless, further studies are been currently addressed to decrease the iron leaching of Fe-mesostructured materials as S-2 to minimal values

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