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Heterogeneous oxidation of organics from wastewater: Fe-ZSM-5 prepared by different silicon sources

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ABSTRACT

Phenol and its compounds in liquid streams are known to cause acute toxic effects in human. Fe-ZSM-5 (T = TEOS silicon source) and Fe-ZSM-5 (S = Silica sol as silicon source) with 1.2 and 1.02 wt% of iron were prepared by the direct hydrothermal synthesis procedure. These catalysts have been characterized by X-ray diffraction, FTIR, SEM, BET and ICP-OES. The alike XRD pattern, obtained for both the samples, has shown that the inclusion of Fe species into the ZSM-5 did not provoke detectable changes in their MFI structure. FTIR investigations of the samples proved the presence of Fe both in framework and extra framework. The total iron content was determined by ICP. The catalytic activity of Fe-ZSM-5 (T) and Fe-ZSM-5 (S) with H_2O_2 decomposition into hydroxyl radical and phenol removal strongly depended on the iron incorporation into ZSM-5 prepared with different silicon sources. The highest activity with phenol removal for the sample Fe-ZSM-5 (T) containing more iron in the framework was noted. The lower activity of Fe-ZSM-5 (S) in this catalytic oxidation process is most likely related to the less content of iron and lower BET surface area. The quantity of leached Fe is not much different for both the synthesized catalysts.

Keywords: Iron; ZSM-5; Phenol; Catalytic Oxidation; Wastewater

1. Introduction

Phenol is an important industrial reagent commonly used in the production of pharmaceuticals such as paracetamol, antiseptic and many others like soap, resins and polymeric plastic [1]. Therefore, the presence of phenol in the industrial as well as domestic waste is unavoidable. Several methodologies, including adsorption, biological treatment, membrane filtration, catalytic oxidation and advanced oxidation processes (AOPs) have been used for the treatment of phenolic pollutants from aqueous waste streams [2]. Among all, AOPs have been successfully used for the abatement of phenolic wastes. A number of AOP procedures such as Fenton oxidation, ozone oxidation and UV (photo) oxidation are usually used for the degradative removal of organic compounds of waste water [3,4]. Fenton oxidation process due to its ease and efficiency was found to be an adorable method as compared to other AOP protocols. However, the Fenton oxidation method is associated with troubles such as sludge production and continuous supply of oxidant as it is a homogeneous process. On the other hand, although, the Fenton-catalytic process due to its straightforwardness, heterogeneity, moderate operational conditions and versatility, could be well thought-out as a beneficial process for treatment of organic pollutant wastes, by using a catalytic adsorbents family of Fe-ZSM-5 zeolites [5]. In recent years, various types of catalytic zeolites such as Cu-ZSM-5, Fe-ZSM-5 Mo-ZSM-5 and silica supported have been used for the destruction of organic compounds containing wastes [6,7]. Among all, Fe-ZSM-5 due to the catalytic properties and their heterogeneity as well as no sludge production have been used for the treatment of organic wastes [8–10]. Furthermore, Fe-ZSM-5 due to high surface area, controlled availability and catalytic activity has a higher potential for treatment of waste water as compared with iron compounds [10–12].

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In the Fenton catalytic oxidation process, degradation of organic compounds from the waste stream is based on the generation of very reactive free hydroxyl radicals. The removal rate of organics from wastewater is accelerated by using Fe-ZSM-5 micro sized particles as catalyst in the AOP heterogenous process. For this, Fe-ZSM-5 zeolite catalyst particles were synthesized and potential of synthesized zeolites is studied for the removal of phenol during the Fenton catalytic oxidation process.The objective of the present work, was to study the effect of different silicon sources on the hydrothermal synthesis of Fe-ZSM-5 and consequently, on the catalytic properties of synthesized materials toward the degradation of phenol in wastewater.

2. Materials and methods

2.1. Materials

$FeCl_3.7H_2O$, silica sol, tetraethylorthosilicate (TEOS), $NaAlO_2$, NaOH, TPAOH, H_2O_2, phenol and chloroform were purchased from Sigma-Aldrich (Sigma Aldrich, USA). Phenol reagent 1 and phenol reagent 2 were obtained from Hach UK. The main equipment used in this study was an autoclave supplied by thermo scientific, which auto temperature and stirring control. Hach spectrophotometer was used for the determination of phenol. Metroohm 706 pH meter was employed for controlling pH.

2.2. Methods

2.2.1. Synthesis of Fe-ZSM-5 catalyst

ZSM-5 zeolite was synthesized by using the following materials. Silica sol. (SiO_2 40%)/TEOS, sodium hydroxide (NaOH), sodium aluminate ($NaAlO_2$), H_2O, tetrapropylammonium hydroxide (TPAOH 1 molar solution) and $FeCl_3.7H_2O$ were utilized to prepare Fe-ZSM-5 according to method as mentioned in the previous literature [13,14]. In the current study, Fe-ZSM-5 was formed by dissolving 0.7481 g of $NaAlO_2$ and 1.5968 g of NaOH in distilled H_2O in one plastic boat.

And 30 ml of silica sol, 6 ml of TPAOH were taken in a beaker and 1.0 g of iron salt dissolve in distilled water. The both dissolve solutions were introduced drop wise into the silica sol while stirring continuously. The molar composition of the synthesis mixture was kept; 1 Al_2O_3:50.4 SiO_2: 6.2 Na_2O: 1.5 TPAOH: 1 Fe_2O_3: 1248 H_2O. The gel mixture was permitted to age at 50°C temperature with 200 RPM rotation in an incubator for 24 h. The gel solution was then moved to steel autoclave lined with Teflon for hydrothermal reaction at 180°C for 48 h under autogenous pressure. After the hydrothermal reaction time of two days the product was gathered followed by filtration and washed until the pH of filtrate reached 8.0. The product material was dried in oven at 105°C for 5 h. The dried porous material was calcined at 550°C for 6 h and thorough characterization was performed, the overall procedure used is according to our previous work [14]. The sample prepared with silica sol was named as S while the sample prepared with TEOS was named as T.

2.2.2. Characterization of synthesized catalysts

The overall characterization procedure is similar to our previous work [14]. Breifly, described as, A Rigaku D/Max-2500 X-ray diffractometer with Cu K_α having Ni filter was used to study the crystalline and the MFI structure of prepared materials. The scanning speed of 3°/min was applied to gather the diffraction patterns between 2Θ angles of range 5 to 50°. To identify the presence of double ring characteristic peaks of ZSM-5 a Perkin Elmer Fourier transform infrared (FTIR) spectrometer was applied with KBr pellets. For this puepose 60 added scans at 2 cm^{-1}resolution were recorded. The ZSM-5 zeolite surface morphology was studied by scanning electron microscopy (SEM) (Hitachi S-4800, Japan). The dried catalysts were finely ground and coated with gold-platinum alloy by ion sputtering with the aid of ion sputter (E-1045 Hitachi). The micrographs were then taken. In order to measure BET surface area, the N_2 adsorption and desorption isotherms were measured with the Micromeritics TriStar II 3020 at 77 K. The catalysts were outgassed for 3 h at 300°C in N_2 atmosphere before the measurements. The total surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method. The content of Fe in the catalysts was measured with a Perkin Elmer (Optima 7300 DV) inductively coupled plasma optical emission spectrometer (ICP-OES). Both the samples were dissolved in HF and neutralized with $NaBO_3$ before analysis. The actual concentration of the Fe in the prepared ZSM-5 samples was obtained from the working calibration curve generated from the four standard solutions of Fe. The TOC was monitored by employing TOC-V_{CPH} (Shimadzu).

2.2.3. Fenton catalytic Process for phenol removal

The performance of prepared Fe-ZSM-5 catalysts was checked in the Fenton oxidation process of phenol removal from wastewater. The batch experiments were carried out in a 500 ml, glass beaker at room temperature with the aid of continuous, controlled magnetic stirring at the speed of 200 RMP. The effect of reaction time and type of catalysts on removal of phenol was evaluated at pre-optimized conditions Fenton oxidation process, including Fe-ZSM-5 dosages of 1.0 g/L, pH of 5 and H_2O_2 concentration of 300 mg/L. The concentration of phenol was measured using UV–vis spectrophotometer (HACH) by measuring the absorption at a wavelength of 460 nm using Hach Program 2900 Phenols. The estimated detection limit for program number 2900 is 0.001 mg/L phenol [14]. The concentration of hydrogen peroxide before and after the reaction was measured by iodometric titration.

2.2.4. Iron leaching studies

After the catalytic process for phenol removal, the aqueous solution was filtered at room temperature. After that, the content of the iron metal in the filtrated solution was determined by UV-Vis spectrophotometer (HACH) at a wavelength of 510 nm using Hach Program 2165.

2.2.5. The prepared catalysts stability determinations

The stability of the synthesized samples was tested as follows: the solid material was recovered from the reaction mixture solution after the reaction time by filtration. It was then calcined at 500°C for 3 h in order to remove any phenol species left over adsorbed. Finally, this material is applied for catalytic test again at the same reaction conditions mentioned in Fenton catalytic process section. The whole procedure was repeated 3 times.

3. Results and discussion

3.1. Characterization of synthesized catalysts

The X-ray diffraction pattern, FTIR absorption peaks and SEM images of the synthesized Fe-ZSM-5 microparticles are shown in Figs. 1–3. As shown in Fig. 1, the diffraction of prepared zeolite particles prepared by silica sol (S) and TEOS (T) indicated the expected peaks for the ZSM-5 characteristics at the 2(Θ)angle of 8 and 23. The well diffracted peaks show the excellent crystallinity of both the materials [15,16]. Similarly Fig. 2 shows the FTIR spectrum of the sample (S) and (T), respectively. The ZSM-5 zeolite has characteristic 5 membered double ring peak at the wavenumber of 450, 550, 790 and 1000 cm^{-1} [17,18] which is clearly visible in the spectra of both the samples. Hence, it is said confidently that by changing the silicon source there is no much difference in the overall formation of Fe-ZSM-5, however a little different is appeared in the peak shapes and area, which may be due to more or less inclusions of iron content by varying the silica source. This can be explained in the fact that the silica sol is the most polymerize form of silica in contrast to TEOS which has a shorter unit length.

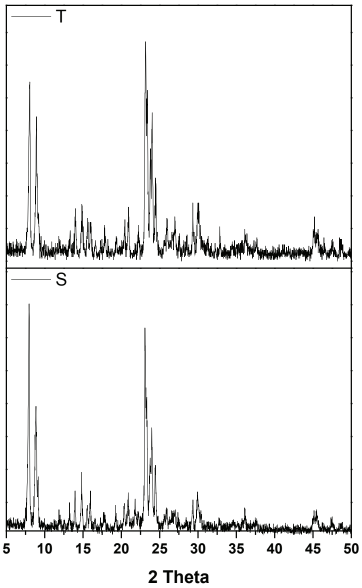

Fig. 1. XRD diffraction pattern collected at room temperature of (*T*) Fe-ZSM-5 prepared with TEOS silicon source (S) Fe-ZSM-5 prepared with silica sol.

It will be further identified by SEM and by applying as catalyst for Fenton oxidation. The morphology and crystallite size of the synthesized catalysts for sample (S) and (T) are presented in Fig. 3. As highlighted in Fig. 3, the sample (S) has smaller crystal size than the sample T. The coffin shaped crystals are intergrown with each other are visible, while more sharped edged square and rectangular crystals are shown in the sample prepared with TEOS. The BET surface area of (T) sample 310 m^2/g is also higher than (S) sample 290 m^2/g, the observe BET surface area and pore volume for the synthesized particles are within the range of ZSM-5 already published [10,19].

This is may be due to the fact that silica sol is a polymeric form of silica, while, tetraethylorthosilicate has a short length monomer unit. The effect of different morphology and BET surface area on the degradation of organics is shown in the next section.

3.2. Fenton oxidation: removal of phenol from synthetic liquid

The power of hydrogen peroxide as oxidizing agent is familiar for the catalytic oxidation of phenol [6]. It is also established that these oxidizing properties in case of liquid phase (as is our concern) are further enhanced by the formation of different radicals like as hydroperoxyl, and hydroxyl, whose generation rate is notably improved in the presence of metals like Fe, Cu, Mn and others. Moreover, it was proved

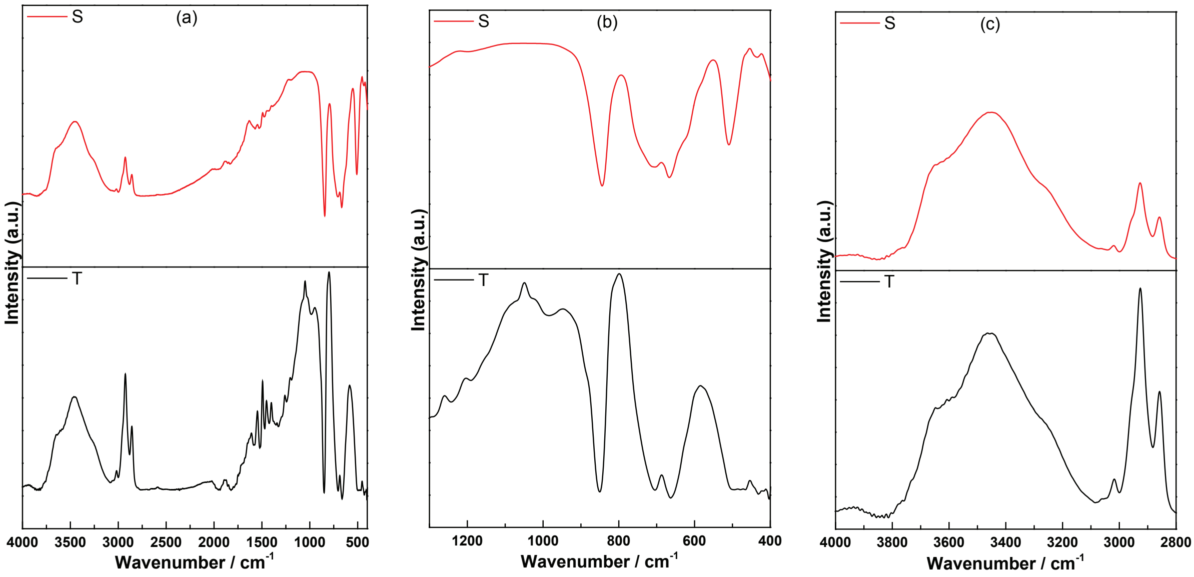

Fig. 2. FTIR spectra of both the materials (a) complete spectrum, (b) finger print region and (c) hydrogen bonging/OH stretching region.

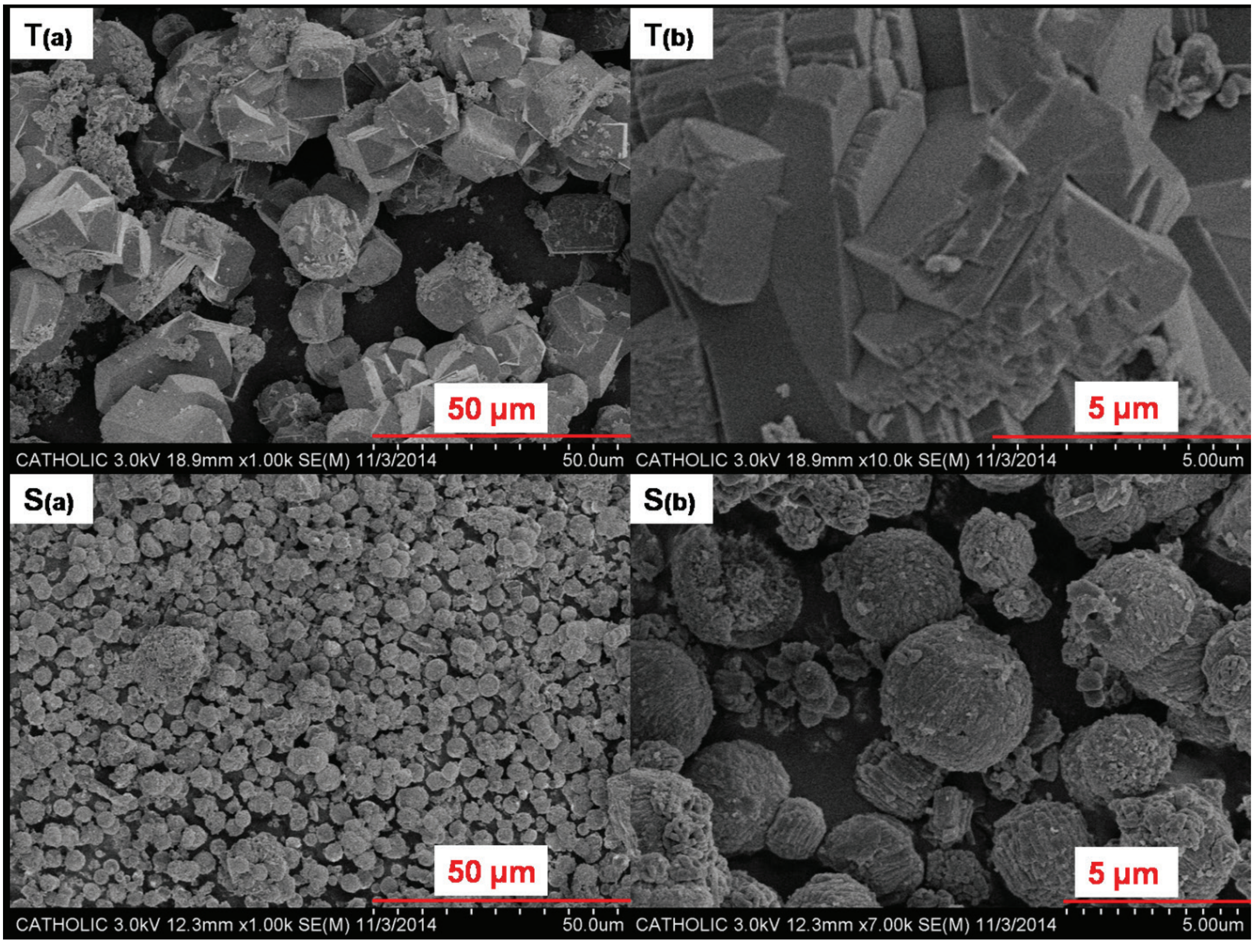

Fig. 3. SEM images of the prepared catalysts T(a) and (b) images of sample prepared with TEOS at 50 and 5 micron, and S(a) and (b) images of sample prepared with silica sol at 50 and 5 microns.

by the researchers that without the presence of catalytic metal the conversion of oxidant (H_2O_2) to powerful oxidizing hydroxyl radical is only 15%, while this ratio can be increased up to 90% with the aid of catalyst [20]. This represents the usefulness of iron species present in the ZSM-5 to encourage hydrogen peroxide transition for the configuration of free hydroxyl radicals in dissimilarity with the very slower decomposition privileged in the non presence of a catalyst. Fenton, oxidation experiments were performed to evaluate the catalytic activity of different prepared Fe-ZSM-5 catalysts. All experiments were performed three times and the Figures show average of three values.

3.3. Catalytic activity of the Fe-ZSM-5 zeolites for the Fenton oxidation of phenol in solutions

Two catalytic materials with ZSM-5 structure (MFI) having contents of Fe different from each other caused by different silic on sources have been prepared as mentioned in the materials and methods section and applied for the catalytic wet oxidation of phenol solutions in the existence of hydrogen peroxide. These materials were experienced with the purpose of finding highly active materials in terms of phenol destruction followed by a minimum possible leaching of iron from catalyst into the solution. The catalytic run of these samples for phenol oxidation at room temperature is shown in Fig. 4(a). The results show that the activity of different materials is closely bound to the quantity of iron incorporated into the zeolitic material. Nevertheless, after 24 h of reaction time, the both catalysts represent the complete abatement of phenol from the reaction mixture (results not shown). Moreover, these results were obtained using just 300 mg/L of hydrogen peroxide, in oppose to the work of other researchers described in literature, who used an excess of hydrogen peroxide oxidant [20]. Fig. 4(a) also indicates the rapidness of chemical reaction in the reaction mixture during the first 5 min. The catalyst T showed the fastest activity with removal efficiency of 60% in the first 5 min while the catalyst sample *S* has catalytic efficiency of 53% for the first 5 min. Fig. 4(b) shows the improvement of hydrogen peroxide decomposition into hydroxyl radicals with the catalytic materials ultimately caused by the different content of iron species present within the catalytic materials. Since, the sample T has an iron content of 1.2 wt% and sample S has 1.05 wt% of iron as listed in Table 1. Therefore, these above mentioned results are in support with the effect of the catalytic metal content (Fe) on the degradation efficiency of the different zeolitic materials (T and S samples) displayed in terms of phenol removal in Fig. 4(a).

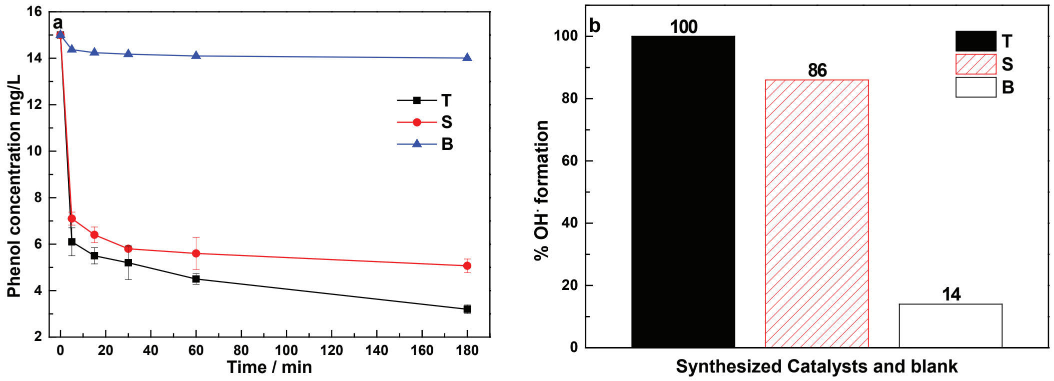

Fig. 4 (a) Phenol removal at different time interval using 1.0 g/L catalyst, 300 mg/L H_2O_2, pH 5 with continuous stirring for samples, (T) Fe-ZSM-5 prepared with TEOS, (S) Fe-ZSM-5 prepared with silica sol, (B) blank (no catalyst added). (b) Hydroxyl radical formation in the reaction mixture after 3 h having no phenol.

Table 1
Physicochemical properties of catalysts

Catalyst	Textural properties		Initial gel composition	Fe-ZSM-5 composition	Fe (wt %)
	BET (m^2/g)	$V_{T(pore)}$ cm^3/g	Si/Fe	Si/Fe	
T	310	0.094	13.84	30.0	1.20
S	290	0.131	13.84	34.3	1.05

Table 2
Leaching and catalytic properties of catalysts

Catalyst	Leaching of iron test				TOC reduction
	Iron in catalyst (mg)	% leached iron			% After 180 minutes
		Fresh	Cycle-1	Cycle-2	
Fe-ZSM-5(T)	12.0	1.00	0.95	0.91	19.97
Fe-ZSM-5(S)	10.5	1.43	1.35	1.20	16.58

Moreover, in order to affirm, a blank catalytic test is also performed in the presence of H_2O_2 while in the absence of prepared catalyst represented for phenol removal in Fig. 4(a) and for hydrogen peroxide decomposition in Fig. 4(b). From this blank catalytic study it is evidence that the presence of catalyst increases notably the peroxide decomposition, confirming the catalytic role of iron in a reaction mixture for the removal of phenol from liquid stream solutions.

The amount of iron leached out from catalyst into the liquid solution after 3 h of reaction time has been determined for the differently prepared zeolitic materials is shown in Table 2. It is gladly seen that the stability of iron species is not much different in both materials. But a little more leaching is observed for sample S than T. This gives an idea about the different environment of Fe species within prepared zeolite. This different environment of Fe is explained with the help of FTIR results in Fig. 2. From the FTIR studies mentioned in the published data [17,18] the bands at 3500 and 3680 cm^{-1} are assigned to hydroxyl nests and extra framework *T* atom OH group also additional bands at 2880 and 2920 cm^{-1} are due to the extra framework presence of Fe in ZSM-5. From Fig. 2, it is obvious that in sample T hydroxyl nest and T atom OH bands intensity decreases as compared to sample S in contrast, more intense peaks at 2880 and 2920 cm^{-1} appears for the sample S over the sample T evidenced that more extra framework iron is present in sample S. The FTIR findings support well the leaching behavior of Fe species.

A more emphasis was given on the reusability of the Fe-ZSM-5 materials. Both Fe-ZSM-5(T) and Fe-ZSM-5(S) were used twice at room temperature, with the findings being showed in Fig. 5. The catalytic activity in terms of phenol removal is somewhat varied after 3 h of reaction time for the fresh and recycled catalysts. Conversely, alike leaching behavior of Fe species for the freshly prepared and regenerated catalysts is easily observed (Table 2). The % leached content of Fe for both of the synthesized catalysts are lower than already reported [3] This behavior is may be due to the on surface readsorption of iron species as described in

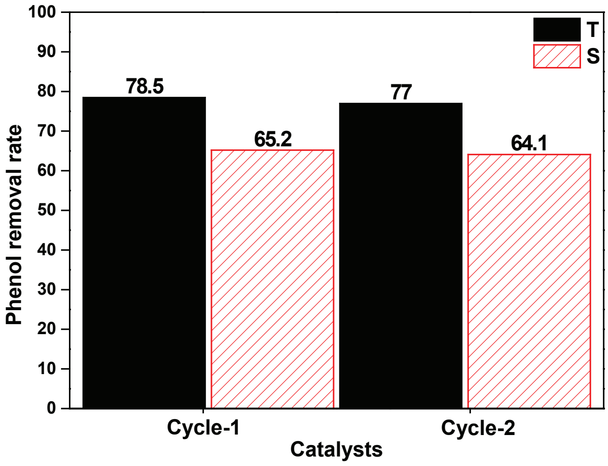

Fig. 5. Stability of Fe-ZSM-5 catalysts, phenol removal of used catalysts at reaction conditions: sample volume = 500 ml, phenol concentration = 15 mg/L, H_2O_2 concentration = 300 mg/L, catalyst concentration = 1 g/L, reaction time = 3 h at room temperature for both cycles.

literature [20]. It is further evidenced that after twice reuse, there is a minimal decrease in the activity of catalyst prepared by TEOS in comparison to the catalyst synthesized with silica sol, although the stability of the sample S is not disappointing.

4. Conclusions

Advance oxidation process (AOP) for phenol in liquid samples with Fe-ZSM-5 prepared with TEOS as a silicon source having a moderate amount of iron (1.2 wt%) is described as the best catalyst for the oxidative removal of water organic pollutants in comparison with the other synthesized catalyst. This promising catalyst has viable properties like usage at pH 5, 60% removal in just 5 min, 80% removal in 3 h, stability without any structural loss for reuse and negligible leaching of catalytic iron.

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References

[1] A.P. Annachhatre, S.H. Gheewala, Biodegradation of chlorinated phenolic compounds, Biotechnol. Adv., 14 (1996) 35–56.

[2] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard. Mater., 160 (2008) 265–288.

[3] M. Hartmann, S. Kullmann, H. Keller, Wastewater treatment with heterogeneous Fenton-type catalysts based on porous materials, J. Mater. Chem., 20 (2010) 9002–9017.

[4] N. Remya, J.-G. Lin, Current status of microwave application in wastewater treatment—A review, Chem. Eng. J., 166 (2011) 797–813.

[5] N. Muhd Julkapli, S. Bagheri, S. Bee Abd Hamid, Recent advances in heterogeneous photocatalytic decolorization of synthetic dyes, Sci. World J., 2014 (2014) 692307.

[6] F.J. Rivas, S.T. Kolaczkowski, F.J. Beltran, D.B. McLurgh, Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts, J. Chem. Technol. Biotechnol., 74 (1999) 390–398.

[7] W. Kujawski, A. Warszawski, W. Ratajczak, T. Porębski, W. Capała, I. Ostrowska, Removal of phenol from wastewater by different separation techniques, Desalination, 163 (2004) 287–296.

[8] K. Fajerwerg, H. Debellefontaine, Wet oxidation of phenol by hydrogen peroxide using heterogeneous catalysis Fe-ZSM-5: a promising catalyst, Appl. Catal. B: environ., 10 (1996) L229–L235.

[9] S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola, G. Vlaic, Structure and reactivity of framework and extraframework iron in fe-silicalite as investigated by spectroscopic and physicochemical methods, J. Catalysis, 158 (1996) 486–501.

[10] R. Joyner, M. Stockenhuber, Preparation, characterization, and performance of Fe−ZSM-5 catalysts, J. Phys. Chem. B, 103 (1999) 5963–5976.

[11] M. Handa, Y. Lee, M. Shibusawa, M. Tokumura, Y. Kawase, Removal of VOCs in waste gas by the photo-Fenton reaction: effects of dosage of Fenton reagents on degradation of toluene gas in a bubble column, J. Chem. Technol. Biotechnol., 88 (2013) 88–97.

[12] P.J. Smeets, J.S. Woertink, B.F. Sels, E.I. Solomon, R.A. Schoonheydt, Transition-Metal ions in zeolites: coordination and activation of oxygen, Inorg. Chem., 49 (2010) 3573–3583.

[13] S. Narayanan, A. Sultana, K. Krishna, P. Mériaudeau, C. Naccache, Synthesis of ZSM-5 type zeolites with and without template and evaluation of physicochemical properties and aniline alkylation activity, Catalysis Lett., 34 (1995) 129–138.

[14] A. Aziz, K. Kim, Investigation of tertiary butyl alcohol as template for the synthesis of ZSM-5 zeolite, J. Porous Mater., 22 (2015) 1401–1406.

[15] J. Wang, H. Xia, X. Ju, Z. Feng, F. Fan, C. Li, Influence of extra-framework Al on the structure of the active iron sites in Fe/ZSM-35, J. Catalysis, 300 (2013) 251–259.

[16] P. Boroń, L. Chmielarz, J. Gurgul, K. Łątka, B. Gil, B. Marszałek, S. Dzwigaj, Influence of iron state and acidity of zeolites on the catalytic activity of FeHBEA, FeHZSM-5 and FeHMOR in SCR of NO with NH_3 and N_2O decomposition, Microporous Mesoporous Mater., 203 (2015) 73–85.

[17] R. Szostak, V. Nair, T.L. Thomas, Incorporation and stability of iron in molecular-sieve structures. Ferrisilicate analogues of zeolite ZSM-5, J. Chem. Soc., Faraday Trans. 1: Phys. Chem. Condensed Phases, 83 (1987) 487–494.

[18] K.P. Dey, S. Ghosh, M.K. Naskar, Organic template-free synthesis of ZSM-5 zeolite particles using rice husk ash as silica source, Ceramics Int., 39 (2013) 2153–2157.

[19] M. Rauscher, K. Kesore, R. Mönnig, W. Schwieger, A. Tißler, T. Turek, Preparation of a highly active Fe-ZSM-5 catalyst through solid-state ion exchange for the catalytic decomposition of N_2O, Appl. Catalysis A: general, 184 (1999) 249–256.

[20] G. Ovejero, J.L. Sotelo, F. Martínez, J.A. Melero, L. Gordo, Wet Peroxide oxidation of phenolic solutions over different iron-containing zeolitic materials, Indust. Eng. Chem. Res., 40 (2001) 3921–3928.