

CATION MODIFIED SILICATES FOR CATALYTIC PRODUCTION OF PHENOL FROM BENZENE

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Abstract

The current work was an attempt to produce phenol from benzene in a one step using Al and Fe modified Silicates. This chemistry would be commercial from industrial point of view with the obtained conversion of benzene to phenol in one step. The preparation of Al and Fe-Silicate have been carried out at 100 °C by the addition of Al and Fe sources to silicate solution and the obtained material were dried at 100 °C over night and calcined at 550 °C. The obtained materials were characterized using X-ray diffraction (XRD) and Infra Red (IR) spectroscopy. The oxidative properties of obtained solids (Al and Fe-Silicates) have been tested in the catalytic oxidation of benzene to phenol at different temperatures. The wide structure characterization of Al and Fe modified Silicates was carried out to establish a correlation between the effects of the addition of the modified silicates on the oxidation of benzene and their structure properties. Best conversion of benzene to phenol was observed for Fe-Silicate sample. A possible explanation of Fe-Silicates activity might be related to the great surface area and acidic properties of this sample in addition to the ability of Fe (III) to be reduced to Fe (II) and vice-versa. The oxidation processes were followed up using HPLC and UV-Vis Spectrophotometer.

Keywords: *Fe and Al Cation modified Silicates; Benzene oxidation; H₂O₂; Phenol and HPLC.*

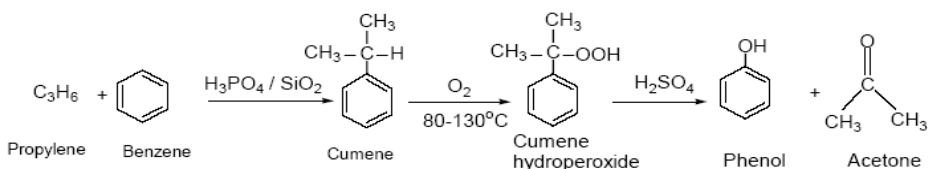
Introduction

Oxidation reactions are of prime importance at an industrial level and correspond to a huge market, for example in the US in 1994, about 31% of the catalytic production of major organic chemicals corresponded to oxidation catalytic processes. Oxidation reactions are widely practiced in industry and are thoroughly studied in academic and industrial laboratories. Catalyzed oxidation reactions are today one of the most dynamic and fruitful field in catalysis. Major achievements were attained in oxidation catalysis. They resulted in the development of many new selective oxidation processes; for example, oxidation of ethylene to acetaldehyde, oxidation of butylenes to maleic anhydride, oxidation of methanol to formaldehyde, etc. These processes have deeply affected the structure of the global chemical

industry. Environmental protection also relies mainly on oxidation reactions. Remarkable results obtained in this field contribute to promote the social image of chemistry which gradually changes from being the enemy of nature to becoming its friend and savior.

Phenol is a valuable intermediate for the synthesis of petrochemicals, agrochemicals (phenoxyacetic acids as a herbicide), and plastics [1, 2, 3]. Phenol is also a disinfectant effective against vegetative Gram-positive and Gram-negative bacteria and certain viruses [3]. In quantity produced, phenol ranks near the top of the list of synthetic aromatic compounds [4]. Global production of phenol was nearly 6.4 million metric tons in 2001, valued at approximately \$4 billion [5-8].

Currently, phenol is produced from benzene by the Cumene process. This process consists of three steps as can be seen in Scheme I.



Scheme I.: Reactions for Cumene process

The first step is the alkylation of benzene with propylene to Cumene in presence of silica-supported phosphoric acid. This reaction can also be performed with Friedel-Crafts catalysts such as aluminum trichloride (AlCl_3) at 100 or 200 °C. Then Cumene is converted to Cumene hydroperoxide in a non-catalytic auto-oxidation reaction. The final step is the acidic cleavage of hydroperoxide into phenol and acetone that is catalyzed by free sulfuric acid AT 60-100°C [2, 5, 7, 8]. Cumene can be produced using either supported phosphoric acid (UOP process) or AlCl_3 (Monsanto process) as alkylation process. The most important drivers for technology innovation are competitiveness and environmental concern. The high amounts of produced acetone in Cumene process are one of the major driving forces to search for new catalytic process, which enable a one step synthesis of phenol without byproducts. Thus, direct introduction of a hydroxyl group into benzene is one of the most challenging tasks in oxidation catalysis.

Other method used for the production of phenol normally, the direct hydroxylation of benzene which performed both in the liquid and gas phase. To

CATION MODIFIED SILICATES FOR CATALYTIC PRODUCTION, ... 29

avoid deep oxidation, an oxygen species of mild reactivity seems to be necessary. One of the routes is the oxidation of benzene with N_2O over ZSM-5 at 573–673 K [9–15]. Recently, iron and chromium containing phosphotungstate salts were reported to be efficient catalysts for the hydroxylation of benzene [16, 17]. Various other catalytic systems involving a vanadium-exchanged heteropolyacid [18] or palladium acetate were also reported to be catalytic precursors for the hydroxylation of benzene [19]. However, the yield of benzene hydroxylation to phenol reported in the literature was relatively low and the as-prepared phenol was not separated. This motivated the present investigation of the reaction, in which the catalyst and reaction conditions were optimized to improve the yield and selectivity of phenol.

In the present work, Fe and Al-modified Silicates were synthesized. Its catalytic behavior was tested in the hydroxylation of benzene with hydrogen peroxide as the oxidant and 36 wt. % acetic acid as the solvent. Optimum reaction conditions for the hydroxylation of benzene to phenol were investigated and are discussed.

Experimental Methods

Chemicals

Na-Silicates, $Al_2(SO_4)_3$, $FeCl_3$, Hydrogen peroxide, Benzene (99.9 %), and Phenol (99 %) were purchased from Aldrich.

Catalyst preparation

Silica incorporated iron and aluminum catalysts were prepared via precipitation of $FeCl_3$ and $Al_2(SO_4)_3$ (99.9+ %) solutions with sodium hydroxide solution as precipitator. The precipitation was carried out in a 2 L precipitated batch maintaining temperatures at 250 K and pH value at 12. The sodium silicate was added into Fe^{3+} and Al^{3+} solutions before precipitation with Fe/SiO₂ weight ratio of 100/50. After precipitation, the precipitate was filtered. The filtered cake was consequently dried at 393 K overnight and calcined at 773 K for 5 h. The obtained samples were composed of 100Al/50SiO₂ and 100Fe/50SiO₂ (denoted as Al-Si and Fe-Si), respectively.

Catalyst characterization

The X-ray diffractograms of various zeolites samples were measured by using a Bruker axs, D8 advance. The patterns were run with Ni-filtered copper radiation ($\lambda = 1.54\text{\AA}$) at 30 kV and 10 mA with a scanning speed of $2\theta = 2.5^\circ \text{ min}^{-1}$.

The FT-IR spectra were recorded on a Bruker (Vector 22), single beam spectrometer with a resolution of 2cm^{-1} . The samples (20 mg/cm^2) were ground with KBr as a tablet and mounted to cavity of the instrument while flushing with nitrogen gas. Pyridine (10 mm pressure) was admitted into the cell and equilibrated with the sample for 1 h. Excess pyridine was then pumped out before recording the spectra. In this way, pyridine was pumped out at 100, 150, 200 and 250°C and the calculated data are represented in table 1.

The nitrogen adsorption isotherms were measured at -196°C using a conventional volumetric apparatus. The specific surface area was obtained using the BET method.

Scanning electron micrographs were obtained using a Joel scanning microscope model JSM5410. Samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold.

Catalytic activity

The catalytic activity of the prepared materials was examined in the oxidation of benzene to phenol using H_2O_2 as oxidant and acetic acid as solvent. 0.2 mol of pure benzene was mixed with 0.45 mol acetic acid and then placed in a round flask conducted to a reflux system under atmospheric pressure. A weighed amount of the synthesized material and 2.5 ml (50 %) H_2O_2 were added to the reaction solution. The reaction was followed by taking samples at different time intervals and then filtered before analysis.

High Performance Liquid Chromatography (HPLC)

The unreacted benzene and the produced phenol as percentages were analyzed by HPLC using at definite time intervals (Dionex p580 pump) equipped with Dionex 202 TPTM C18 column ($4.6 \times 250\text{mm}$) with eluent consisted of a 60:40 Acetonitrile: water mixture and the flow rate was 1 ml/min using UV-detector at wavelength 225 and 254 nm.

Table 1: Catalytic performance of synthesized Al and Fe-Silicates in Benzene conversion and selectivity to phenol

Catalyst	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Benzene Conversion % at different Temperature ($^\circ\text{C}$)				Selectivity % at different temperature ($^\circ\text{C}$)			
			50	75	100	125	75	100	125	150
Al-Si	850	0.277	28	45	47	32	85	95	78	80

CATION MODIFIED SILICATES FOR CATALYTIC PRODUCTION, ... 31

Fe-Si	1240	0.35	63. 4	10 0	88	61	94	98	96	84
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Results and discussion

Structural properties

The structural properties of silica-free and silica-supported catalysts as-prepared were contrasted to illustrate the aluminum and iron–silica interactions. The aluminum and iron phases in catalysts were identified by using XRD, IR and SEM spectroscopy. The XRD patterns of the catalyst samples as-synthesized are presented in Fig. 1. The patterns show that the silica-free exhibits amorphous structure as reported in literatures. The result also implies that iron phase in catalyst Fe-Si is well-crystallized α -Fe₂O₃, which is almost identical with the reference pattern of hematite in line position and relative intensity. Further more, a new diffraction lines at $2\theta = 27.5, 32.5$ which are assigned for the characteristic of Fe₂SiO₄ phase when compared with the instrument Fe-silicate standards. On the other hand The XRD patterns of aluminum shows the characteristics diffraction lines of crystalline Al-Silicate as that of zeolites.

IR spectra of various samples

The FT-IR spectra of Fe-Si and Al-Si calcined at 773 K are shown in Fig. 2 in the range 450-1700 cm⁻¹. The IR spectrum of Fe-Silicate shows bands at 1130, 1062, 937, 790, 612 and 458 cm⁻¹, which are assigned to different vibrations of tetrahedral and framework atoms in silicate structure [20]. The bands at about 1130 and 464 cm⁻¹ are due to internal vibrations of (Si, Al)O₄ tetrahedra of Silicate structure, whereas the bands at about 1062, 790, and 612 cm⁻¹ are due to vibrations related to external linkages between tetrahedra and hence sensitive to framework structure[21,22]. Furthermore, the appearance of a new absorption band at 937 cm⁻¹ may be related to stretching vibrations of Fe-O bond.

IR spectra of hydroxyl region

Fig. 3 shows the FTIR spectra of Al and Fe-Silicate in the hydroxyl region. The Al-Si sample exhibits five bands at 3736, 3695, 3628, 3598 and 3520 (shoulder) cm⁻¹, similar to what is observed in most zeolite structures. The bands at 3736 and 3695 cm⁻¹ are due to isolated silanol groups and hydroxyl groups attached to silica–alumina- containing species, respectively. The structural acidic bridging Al–OH–Si groups (Brønsted acid sites) exhibit two peaks at 3628 and 3598 cm⁻¹, as observed in the case of other high-silica, large-pore zeolites such as mordenite [23, 24] and ZSM-12 [25]. These peaks are assigned [23, 24] to bridging hydroxyl groups vibrating in the main 12-ring channels and in small six- or eight-membered ring channels, respectively.

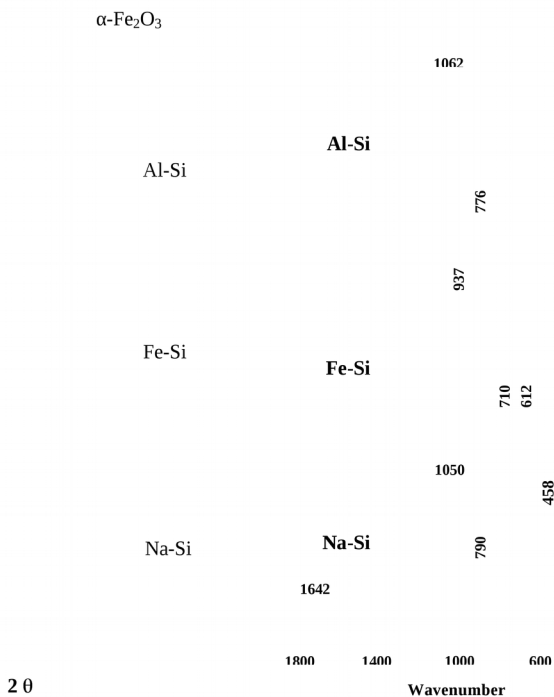


Fig. 1. XRD patterns of calcined Fe-Silicate at 823 K in comparison with the parent Na-Silicate

Fig 2. IR Spectrum of the as synthesized Fe and Al-Silicate in comparison with Na-Silicate calcined at 823 K

The FTIR spectrum of Fe-Si exhibits bands at 3738, 3700 (sh), 3650 (broad), 3615 and 3520 (broad) cm^{-1} . These bands are assigned to similar vibrations as for Al-Silicate. However, due to the larger size and higher electronegativity of Fe compared to Al, the Fe–O bond lengths are larger than that of Al–O. This will cause the bands Fe(OH)Si (3650 and 3615 cm^{-1}) to shift to higher wave numbers as compared to the Al(OH)Si (3628 and 3598 cm^{-1}) bands.

The surface concentration of Brønsted and Lewis acid sites in our samples was determined [26-29] from the integrated areas of the bands relative to adsorbed pyridinium ions (1545 to 1547 cm^{-1}) and pyridine coordinated to Lewis sites (1455 to 1450 cm^{-1}), respectively, appearing in FTIR spectra recorded after pyridine adsorption at 423 K. The relative strength of acid sites was estimated from the integrated areas of these bands in spectra recorded after evacuation of the probe at progressively higher temperature [29]. The absolute values of Lewis acid site (LAS) and Brønsted acid site (BAS) concentrations per gram of dry catalyst, calculated by employing the integrated molar absorption coefficients obtained in ref. 27, are reported in Table 2.

Table 2: Surface concentration of Brönsted acid (BAS) and Lewis (LAS) sites determined through FTIR analysis of adsorbed pyridine at 423 K

Catalyst	LAS/ $\mu\text{mol g}^{-1}$	BAS/ $\mu\text{mol g}^{-1}$
Fe-Si	367	341
Al-Si	320	462

SEM

The influence of amorphous substitution on the morphology of the calcined Fe-Si and Al-Si materials was studied by SEM. Incorporation of heteroatom to amorphous structure as in silicate may lead to the increasing of crystallinity. The SEM pictures of the synthesized Al and Fe-Silicates samples are presented in Fig. 3. All pictures show non-homogeneous particle size distribution. The presence of elongated crystallites, with varying sizes could clearly be discerned for Hematite species form upon the calcination of Fe-Si. On the other hand, the aspect ratio of the crystallites seems to increase in case of Al-Si.

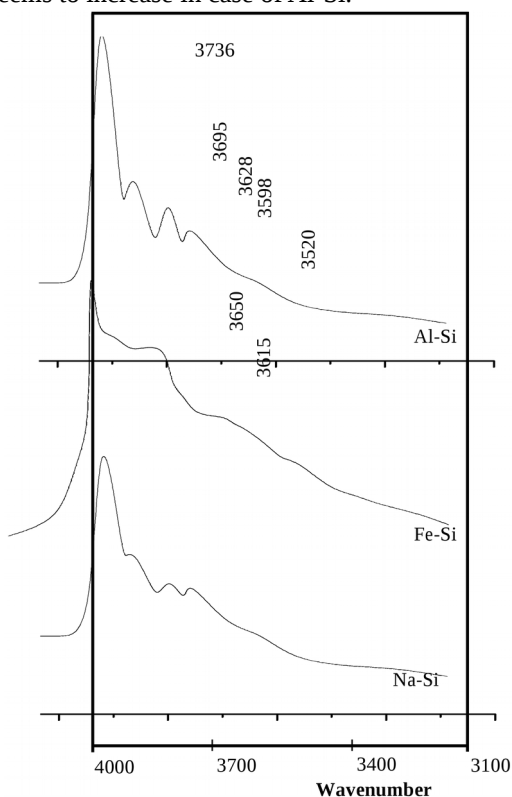


Fig 3. IR Spectrum of the as synthesized Fe and Al-Silicate in comparison with Na-Silicate calcined at 823 K in the hydroxyl region

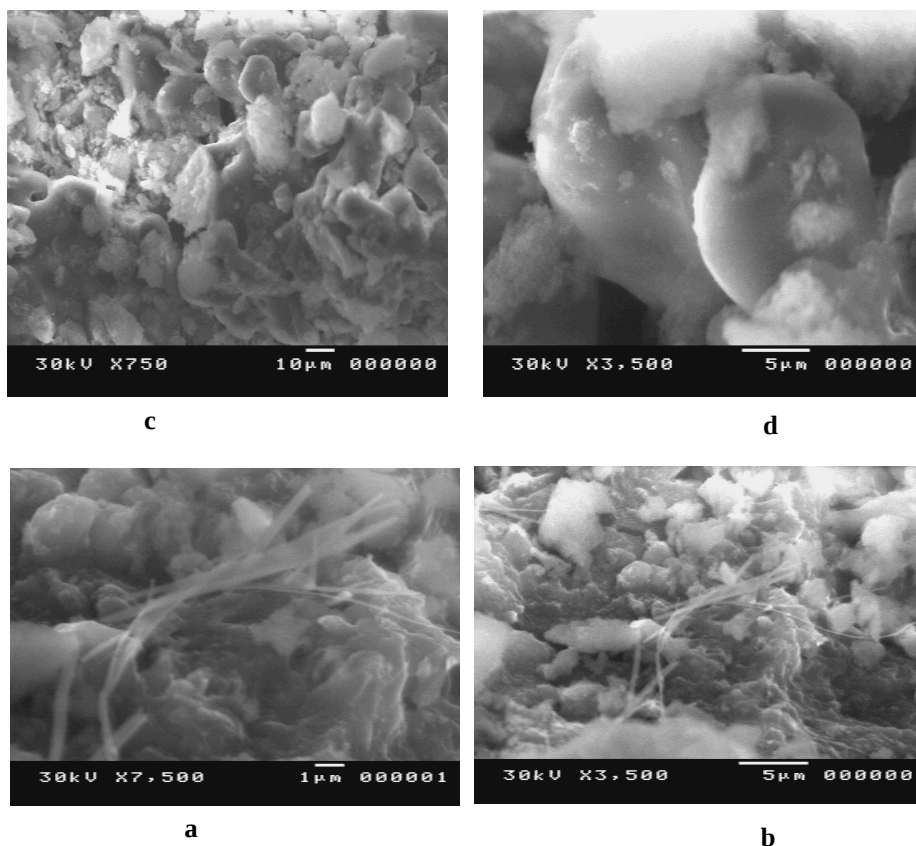


Fig. 3. SEM pictures of different magnification obtained for the synthesized and calcined at 823 K(a,b) Fe-Silicate and (c,d) Al-Silicate

Surface area

The Nitrogen adsorption-desorption isotherms indicate that the values of surface area increases with modification of silicate with Al and Fe cations and the obtained surface areas were depicted in Table 2. The data also indicate that modification with Fe exhibits the largest surface area when compared with that modified with Al cations.

UV-Vis

The UV-Vis spectra of synthesized Fe and Al-Silicates are shown in Fig. 4. the spectra show a characteristic absorption bands around 256, 265, 275, 333 and 360

nm; the intensities of these bands vary upon calcination from 423 to 823 K. The appearance of these new bands at 256 upon modification with Fe species with increasing intensities (Fig. 4a) after calcination at 823 K, may be associated with ligand to metal charge transfer (CT) that involves isolated four co-coordinated Fe(III) and has been assigned to $t_1 \rightarrow e$ involving Fe(III) in $[\text{FeO}_4]$ tetrahedral [23]. Furthermore, the spectrum of calcined Fe-Silicate shows a small CT absorption band around 283 nm, which is assigned to Fe(III) species in octahedral coordination [24]. The appearance of this species indicates leaching of Fe(III) from the framework during calcination of the synthesized Fe-Silicates. On the other hand, the UV-Vis spectra of Al-Silicate (Fig. 4b) exhibits only one absorption band at 335 nm as that exist in the Fe-Silicate. The appearance of this band might be assigned for Si-O-M bond in the five membered ring characterizing for zeolite structure. Generally, the appearance of some absorption bands in the range from 350 to 430 nm may indicate the formation of minute oxide species formed during calcination of the materials [25].

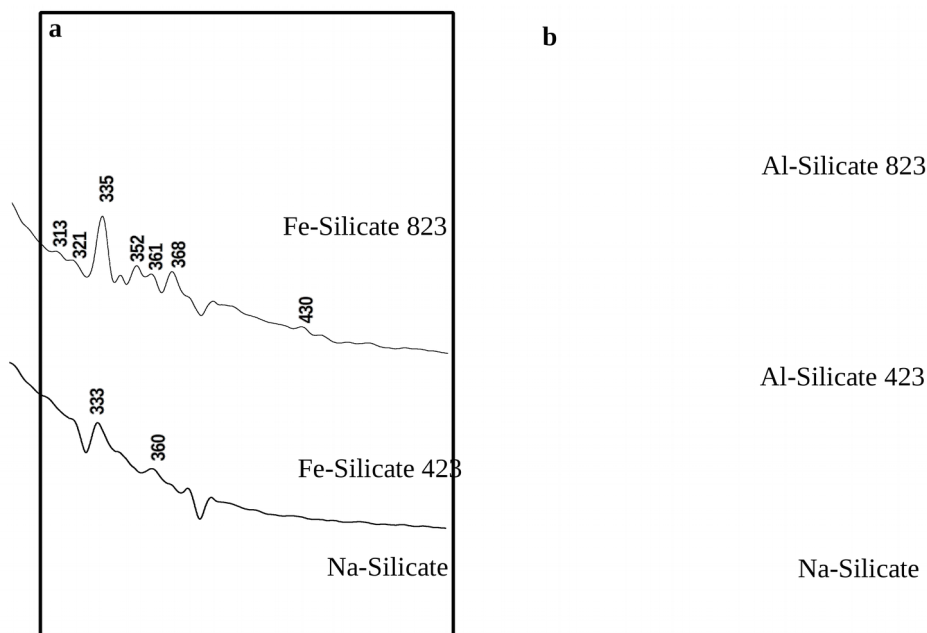


Fig. 4. UV-Vis spectra of synthesized and calcined **a)** Fe-Silicate **b)** Al-Silicate

Oxidation Reaction

The above prepared Fe and Al-Silicates samples were used as catalysts for benzene hydroxylation at different temperatures. The presence of Fe and Al in Silicate matrix is essential for performing the oxidation of benzene to phenol. The oxidation of benzene with H₂O₂ as oxygen carrier material as controlled experiment was carried out prior to the actual heterogeneous catalytic reaction. In the absence of Fe-Si and Al-Si no significant conversion of benzene to phenol was noticed.

Figs 5 and 6 represent a typical time course of the relative conversion % for Fe-Si and Al-Si at different reflux temperatures. All catalysts were able to oxidize benzene to phenol in the space of Ca. 40-80 min time range for Fe-Si and Al-Si, respectively with a higher selectivity (Table 1), but the yield of phenol only reached 45 % with Al-Silicate, which might be a half or less than that obtained using the Fe-Silicate as a catalyst at the same conditions. These data reveal that different Fe species especially $\alpha\text{Fe}_2\text{O}_3$ as detected by XRD are all responsible for the hydroxylation of benzene. Furthermore, there was a significant increase in benzene oxidation with temperature, since the conversion % increase gradually with increasing temperature to reach maximal values (100 %) at 75 °C after 40 min with 98 % selectivity then decrease again for Fe-Si sample as illustrated in Fig. 5 whereas, for Al-Si(45 %) at 100 °C after 80 min (Fig. 6). This finding strongly indicates the effective role of Fe active sites distributed between the surface and silicate matrix.

Effect of temperature.

To investigate the effect of temperature on the yield of phenol, the temperature was varied from 50 °C to 125 °C, while the other parameters being kept constant. The results are shown in Figs. 5 and 6, from which it can be seen that the yield of phenol increased with increasing temperature. The yield of phenol markedly decreased when reaction temperature exceeded 100 °C. The reason for this decrease may lie in the fact that the higher temperatures favored volatilization, formation of higher phenolic members which have been detected by HPLC above 100 °C, the deep oxidation of benzene and the self-decomposition of H₂O₂. Table 1 represents the obtained selectivity of phenol formation. The data reveal that the higher selectivity was displayed by Fe-Silicate at 75 °C when compared with other temperatures.

Generally, the results of activity measurements of Al and Fe catalysts in the oxidation of benzene to phenol by H_2O_2 are reported in Table3, as percentage reactant conversion and percentage selectivity to phenol. The percentage phenol yield, which can be easily calculated as the product of conversion and selectivity, clearly depends on the acidity properties of the catalysts, and in particular on the ratio between the number of LAS and the number of BAS, as shown in Table2 . The reactant conversion is favored by an increase of the LAS/BAS ratio, as observed in previous studies [32] but depends also on the concentration of surface acid sites.

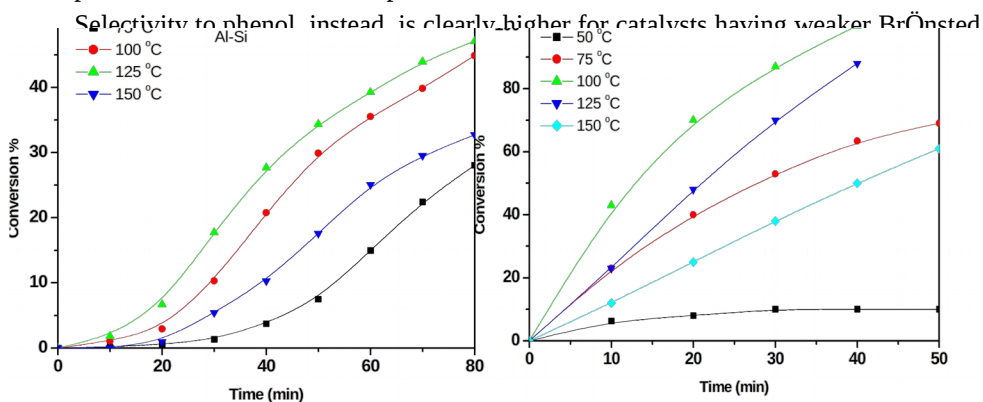
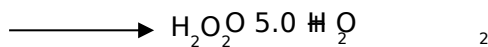


Fig. 6. Benzene to phenol conversion % against time on Al-Silicate

Fig. 5. Benzene to phenol conversion % against time on Fe-Silicate

Effect of Catalyst Concentration.

Figs. 7 and 8 represent the effect of catalysts concentration on the conversion of benzene. From the above Figures it can be seen that the yield of phenol increase with increase the amount of Al-Si catalyst. On the other hand, the marked decrease of the conversion rate was observed with Fe-Si which may be assigned for, the rapid consumption of H_2O_2 . In case of Fe-Si strong effervescence has been observed upon the addition of the catalyst to the reaction mixture which means that H_2O_2 rapidly decomposed to atomic oxygen and water as follows:



On the other hand with Al-Silicate the situation is different, since no significant increase in the decomposition of H_2O_2 upon increasing the catalyst amount which means that the interaction between the catalyst and H_2O_2 is extremely weak. Fig 9 shows the HPLC chromatogram of benzene oxidation. The data indicate the formed

CATION MODIFIED SILICATES FOR CATALYTIC PRODUCTION, ... 39

phenol peak appears at RT = 2.25 min accompanying for that of benzene at RT = 3.75 min.

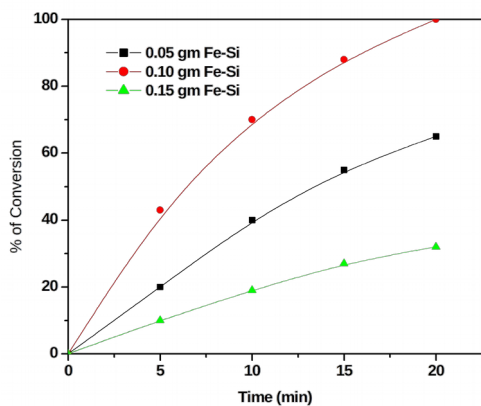


Fig. 7. Effect of Fe-Silicate concentration on the catalytic oxidation of Benzene

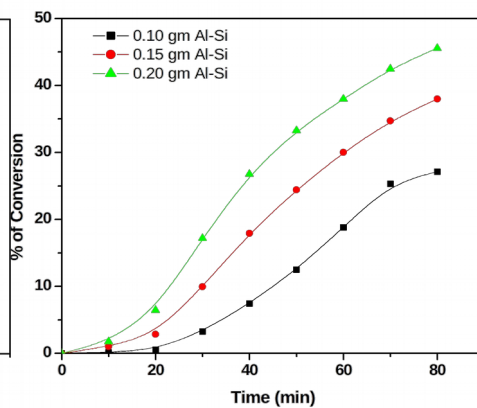


Fig. 8. Effect of Al-Silicate concentration on the catalytic oxidation of Benzene.

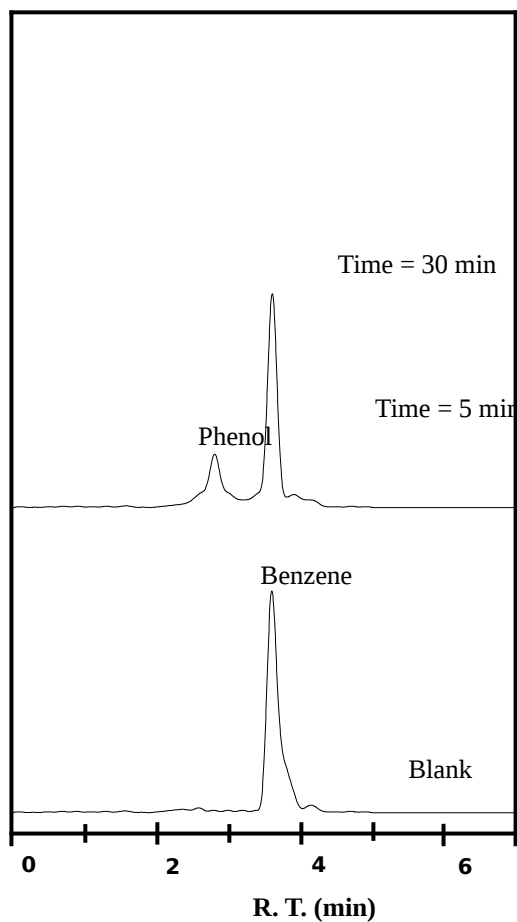


Fig. 9: HPLC chromatograph of Benzene oxidation and concomitant appearance of phenol

Effect of H₂O₂.

In order to evaluate the effect of H₂O₂, different concentrations of this oxidant have been added to the reaction system. Experimental data indicate that the yield of phenol increased with increasing amount of H₂O₂ and reached a maximum at 1.0 and 0.8 mmol H₂O₂ with Fe-Si and Al-Si respectively, the conversion of benzene is directly proportional with the amount of H₂O₂ used. As depicted in Figs. 10 and 11 we can see that the maximum conversion % (100) has been obtained after 15 min with 1.0 mmol H₂O₂ / 0.1 gm Fe-Si at 75 °C, whereas (80 %) was obtained after 80 min with 0.8 mmol H₂O₂ / 0.1 gm Al-Si at 100 °C. it is also noticed that increasing the amount of H₂O₂ increase the amount of detected higher phenolic compounds.

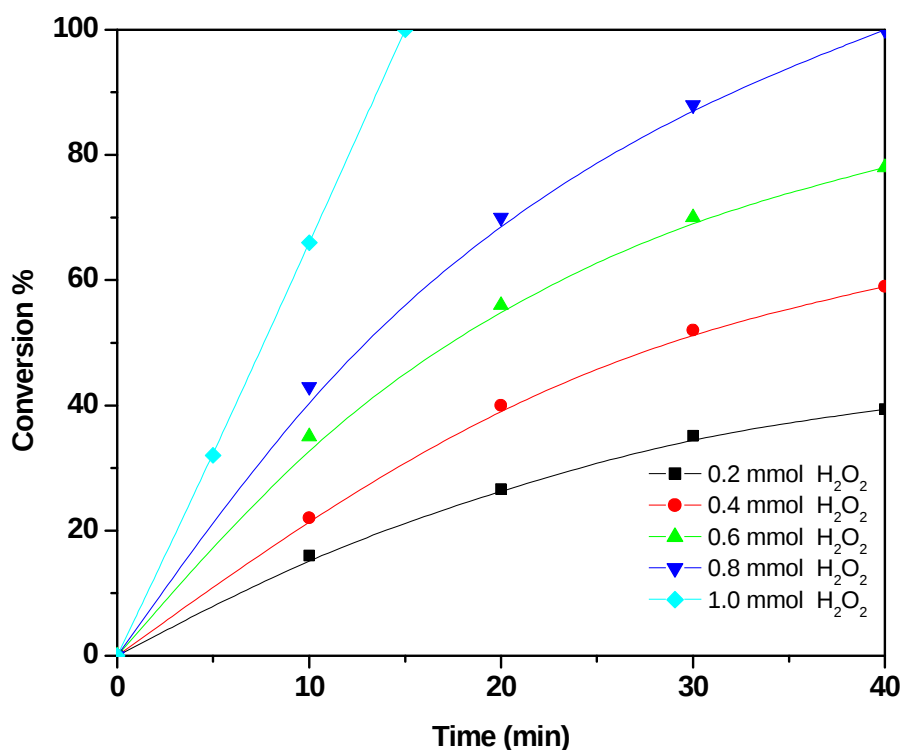


Fig. 10. Effect of H₂O₂ concentration on the catalytic conversion of Benzene to phenol on Fe-Silicate

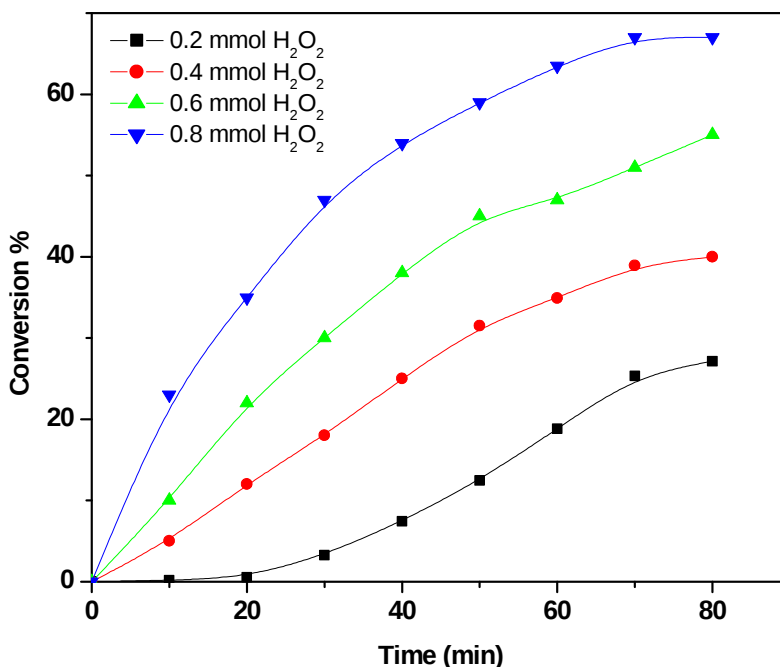


Fig. 11. Effect of H₂O₂ concentration on the catalytic conversion of Benzene to phenol on Al-Silicate

Conclusion

The preparation of Al and Fe-Silicate were achieved using hydrothermal method. The formation of phenol by the catalytic oxidation of benzene with hydrogen peroxide by Fe and Al-Silicate catalysts was confirmed; However, The obtained data proof that Fe-Silicate at 323 K the most suitable catalyst and temperature for the catalytic conversion of benzene to phenol due to High acidity of this sample.

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