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Cation modified silicates for catalytic production of phenol from benzene

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Abstract

In this work, we produced phenol directly from benzene using silicates modified with Al and Fe. The preparation of Al and Fe-silicates was done at 373 K by mixing a silicate solution with Al and Fe sources and the resulting material were dried at 373 K overnight and calcined at 823 K. The calcined materials were characterized using XRD, IR, SEEM and SBET. The oxidative properties of resulting solids (Al and Fe-silicates) were tested in the catalytic oxidation of benzene to phenol at different temperatures. The oxidation processes were followed up using HPLC and UV-Vis Spectrophotometry.

Keywords: Fe and Al Cation modified silicates, Benzene oxidation, H_2O_2, Phenol

1. Introduction

Due to the importance of phenolic compounds in several industries, various researchers have tried to produce phenol by other methods such as benzene oxidation. The consumption of phenolic compounds produced from catalyzed oxidation of benzene reached 31% in the USA in 1994. The process of direct hydroxylation of benzene was done in both the liquid and gaseous phase. Recently, iron and chromium containing phosphotungstate salts were reported to be efficient catalysts for the hydroxylation of benzene [1-5]. However, the yield of benzene hydroxylation to produce 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 for phenol production.

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

2. Materials and methods

2.1 Chemicals

Na-silicates, $Al_2(SO_4)$, $FeCl_3$, hydrogen peroxide, benzene (99.9 %), and phenol (99 %) were purchased from Aldrich.

2.2 Catalyst preparation

Silica incorporating iron and aluminum catalysts were prepared via precipitation of $FeCl_3$ and $Al_2(SO_4)$ solutions with a sodium hydroxide solution as a precipitator. After precipitation, the precipitate was filtered. The filtered cake was dried at 393 K and calcined at 823 K for 5 h. The obtained samples were composed of $100Al/50SiO_2$ and $100Fe/50SiO_2$ (denoted as Al-Si and Fe-Si), respectively.

2.3 Catalyst characterization

X-ray diffraction analysis of various silicates was done using a Bruker axs, D8 advance. The patterns were run with Ni-filtered copper radiation (λ =1.54Å) at 30 kV and 10 mA with a scanning speed of $2\theta = 2.5^o$ min^{-1}. *The FT-IR spectra* were recorded on a Bruker (Vector 22), single beam spectrometer with a resolution of $2cm^{-1}$. *Nitrogen adsorption isotherms* were measured at -196ºC using a handmade volumetric apparatus. The specific surface area was obtained using the BET method. *Scanning electron micrographs* were obtained using a Joel scanning electron microscope Model JSM5410.

2.4 Catalytic activity

In this part, 200 ml of pure benzene was placed in a round flask connected to a reflux system at atmospheric pressure. A weighed amount of the synthesized material and 2.5 ml (50 %) H_2O_2 were added to the benzene solution. The reaction was followed by taking samples at various time intervals and filtering them before analysis.

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2.5 High Performance Liquid Chromatography (HPLC)

The reaction was followed using a HPLC (Dionex p580 pump) at definite time intervals equipped with Dionex 202 TPTM C18 column (4.6 x 250 mm). Its eluent consisted of a 60:40 acetonitrile:water mixture and the flow rate was 1 ml/min using a UV-detector at wavelengths of 225 and 254 nm.

3. Results and discussion

3.1 X-Ray diffraction

XRD patterns (Figure 1) show that the parent silica exhibits an amorphous structure. However, in an Fe-Si catalyst, the iron is well-crystallized as α-Fe_2O_3, which is almost identical to the reference pattern of hematite in both relative intensity and line position. Additionally, new diffraction lines at 2θ= 27.5 and 32.5 could be ascribed to the characteristics of a Fe_2SiO_4 phase when compared with the instrumental Fe-silicate standards. Alternatively, the XRD patterns of aluminum shows the same characteristic diffraction lines of crystalline Al-Silicate as zeolites.

3.1.1 IR spectra of various samples

FT-IR analysis of Fe and Al modified materials calcined at 823 K are shown in Figure 2 in the 450-1700 cm^{-1} range. The spectrum of the Fe modified sample shows bands at 1130, 1062, 937, 790, 612 and 458 cm^{-1} can be ascribed to different tetrahedral vibrations and framework atoms in the silicate structure. Furthermore, the appearance of a new absorption band at 937 cm^{-1} may be related to stretching vibrations of an Fe-O bond.

3.1.2 SEM

Image obtained for Al and Fe-Silicates samples using SEM spectroscopy are presented in Figure 3. The images show that the particle size distribution is non-homogeneous. The existence of elongated crystallites, with different sizes could clearly be discerned for Hematite species formed upon calcination of Fe-Si. Alternatively, the aspect ratio of the crystallites seems to increase in case of Al-Si.

3.1.3 Surface area

Surface area measurements indicate that the values of surface area increase upon modification of silicate with Al and Fe cations, as depicted in Table 1. The data also indicate that modification with Fe produced the largest surface area when compared with materials modified with Al cations.

3.2. Oxidation reaction

The oxidation of benzene with H_2O_2 as oxygen carrier as a controlled experiment was done prior to the actual heterogeneous catalytic reaction. In the absence of Fe-Si and Al-Si, no significant conversion of benzene to phenol was observed. Table 2 shows the relative percent conversion for Fe-Si and Al-Si at different reflux temperatures.

In the investigation of different experimental parameters such as temperature, catalyst doses and amounts of H_2O_2 were done and the resulting data are tabulated in Table 2.

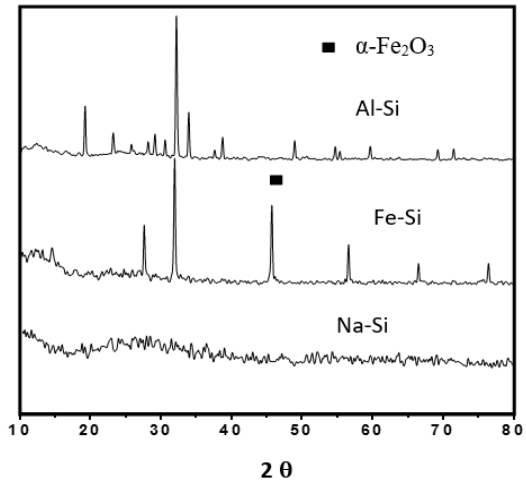


Figure 1 XRD patterns of synthesized materials

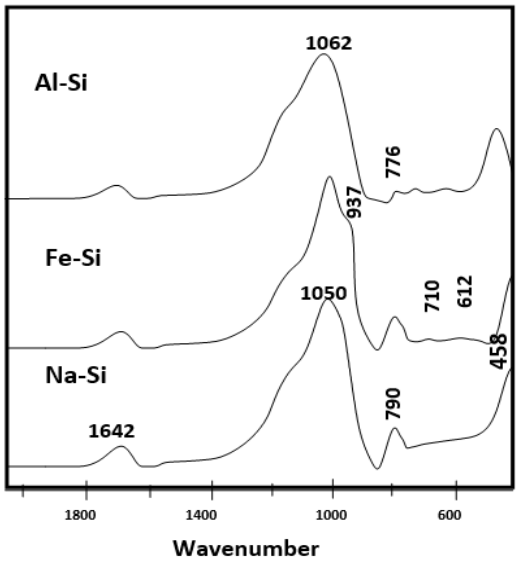


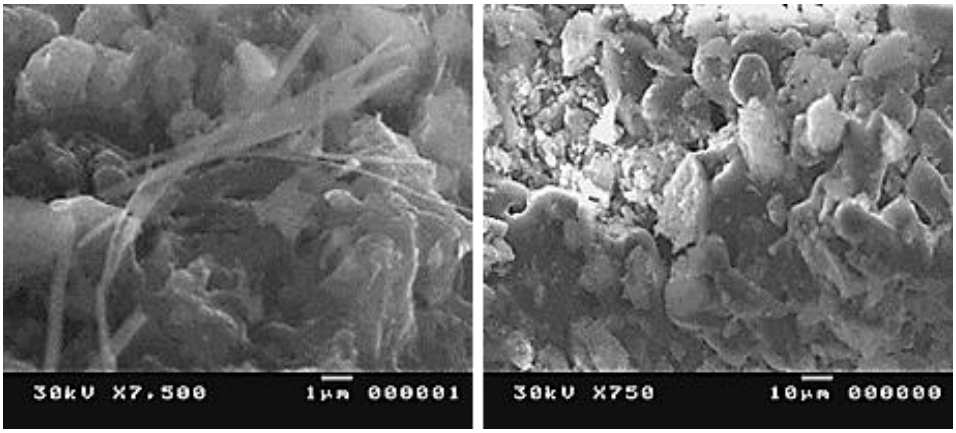
Figure 2 IR spectrum of synthesized materials

Table 1 N_2 sorption results of Al and Fe modified silicates

Sample	BET surface area (m^2/g)
Parent silicate	643
Al-Silicate	850
Fe-Silicate	1240

Table 2 Catalytic performance of synthesized Al and Fe-silicates

Catalyst	S_{BET} (m^2/g)	P. V. (cm^3/g)	Benzene Conversion at different Temperatures (ºC)				Selectivity % at different temperatures (ºC)			
			373	423	473	523	373	423	473	523
Al-Si	850	0.277	28	45	47	32	85	95	78	80
Fe-Si	1240	0.35	63.4	100	88	61	94	98	89	84



(a) (b)

Figure 3 SEM images of the synthesized a) Fe-silicate and b) Al-silicate

4. Conclusion

The preparation of Al and Fe-silicates was achieved using a 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 resulting data showed that Fe-silicate at 323 K offered the most suitable catalyst and temperature for the catalytic conversion of benzene to phenol due to the high acidity of this sample.

5. Acknowledgement

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