Fe-Al-Pillared Clay Used for Conversion of Toluene Through Catalytic Wet Peroxide Oxidation

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Abstract: In the present paper, the wet peroxide oxidation of toluene to benzaldehyde, which is great industrially important, is studied on solid catalyst. The catalyst (Fe–Al) pillared bentonite (Fe–Al/B) is successfully prepared by cation exchanging of purified bentonite (B) with mixed hydroxyl-(Al-Fe) pillaring solution made from hydrolysis of corresponding metal salts with OH/M³⁺ =2.5 (M=Al³⁺, Fe³⁺), followed by calcination at 500°C to convert hydroxyl-Al and hydroxyl-Fe into intercalated polycations. Characterization studies are performed by use of chemical composition, XRD, SEM, TEM and analysis of N₂ adsorption/desorption. The basal spacing (d₀₀₁) and specific surface area of samples increased from 15.3 Å and 91.57cm²/g in the B to 19.4 Å and 229.75cm²/g in the Al–Fe/B. The Fe–Al/B clay catalyst has proved to be promising in toluene oxidation with H₂O₂, selectively forming benzaldehyde under the working conditions. The toluene conversion and the product distribution largely depended on the catalyst and oxidant concentrations and the nature of the solvent. Higher conversion of toluene and greater selectivity for benzaldehyde is obtained with acetonitrile solvent.

Keywords: Pillared Clay, Toluene, Oxidation, Benzaldehyde

1. Introduction

Selective oxidation of hydrocarbons is considerable interest to chemical industries worldwide and still remains a challenge to chemists. Benzaldehyde is the simplest and industrially the most important aromatic aldehyde, it is intermediate in the production of perfumery, pharmaceutical, dyestuff, and agrochemicals. Benzaldehyde is produced exclusively by the wet peroxide of toluene carried out in a single reaction step in the gaseous or liquid phase. Benzaldehyde is easily oxidized to benzoic acid. Generally, wet peroxide oxidation of toluene is realized with air at a temperature ranging from 110°C [1] to 170°C [2] and high pressure “0.5–2.5 MPa” [3] that renders the reaction medium liquid in the presence of a metal-based catalyst. The reaction selectivity for benzaldehyde ranges from about 30% [4] to about 73% [5]. The used of oxygen in deep oxidation lead to the COx product formation, besides, production of benzaldehyde by a traditional techniques lead a multiple problems such as environmental pollution, erosion of equipment. H₂O₂ is an attractive oxidant not solely due to being more active than O₂, but rather to being with H₂O as the only byproduct. In addition, the search for an optimal catalyst with a selectivity corresponding to commercial viability remains elusive. The pillared clay is known to be effective to catalyst partial oxidation of hydrocarbons using hydrogen peroxide; it is easily recycled after reaction. Many research results have shown catalytic activity of pillared bentonite with Fe-Al for organic compound total oxidation in water, by using hydrogen peroxide as oxidant [6], [7], [8] but, little for oxidation of toluene. This paper investigates the synthesis conditions of (Fe-Al) -pillared bentonite clay catalyst and present the catalytic activity of the sample for the oxidation of toluene with aqueous H₂O₂. The influence of the concentration of oxidant and catalyst, nature of oxidant and solvents on the oxidation of toluene is examined.

2. Materials and Experiments

2.1. Catalyst Preparation

The purified samples are obtained by two different methods i.e. simple sedimentation and chemical treatment [9]. The bentonite is dispersed in distilled water in order to obtain a
diluted suspension (0.5 wt.%), the suspension is stirred for 4h at room temperature till complete homogenization then it is introduced into graduate cylinders of a 2L at room temperature. The suspension is centrifuged after a necessary time, according to Stokes' law, to recover the bentonite fractions contain the particles less than 2 µm, the supernatant is removed and the recovered clay is dried at 102°C for overnight. The chemical treatment is carried with the purpose to remove organic matter and iron oxides using method CBD (Sodium Citrate, Bicarbonate and Dithionite) [10]. The purified samples are dried at 102°C for 12h. The Pillaring solutions are prepared separately by dropwise addition of 0.207M and 0.1M NaOH solution to 0.207M and 0.1M of AlCl₃ and FeCl₃ solution, respectively, until obtaining a molar ratio OH/Fe = 2.5, the solutions are aged for one week at room temperature. After the ageing process, the pillaring solution is mixed with mass ratio 50% (Fe³⁺–Al³⁺) and added to purified bentonite suspension with molar ratio (Fe²⁺–Al³⁺)/clay = 10nmol under stirred for 12h. The mixture is allowed reposed overnight at room temperature, then collected by filtration and washed with deionized water until free of chlorides. The solid (Fe–Al/B) is dried overnight and calcined for 2 h at 500°C, ground and sieved.

2.2. Catalyst Characterization

The Analysis of the chemical composition of the purified bentonite is obtained by fluorescence X. The scanning electron microscopy (SEM) and transmission electronic microscopy (TEM) are used to investigate the morphology of purified and pillared clay using JEOL JSM-6400 at 20 kV for (SEM) and JEOL model 1011 at 100 kV for (TEM). X-ray diffractograms of the samples are obtained with a Siemens model D5000 diffractometer using CoK radiation. To maximize the (001) reflection intensity, oriented clay aggregate specimens are prepared by drying clay suspensions on glass slides. Micromeritics ASAP 2010 Instrument is used to determine the specific surface area and porosity of samples.

2.3. Toluene Oxidation

The liquid phase oxidation of toluene is carried out in a two-neck round bottomed flask (50 ml) fitted a condenser and magnetic stirrer. 0.1g of Fe-Al pillared catalyst is added to calculated amounts of toluene and solvent (acetonitrile). When the temperature is raised up to 363K, required amounts of 30% hydrogen peroxide are added to the reaction system dropwise and then the mixture is refluxed for 10h and at atmospheric pressure. The addition of H₂O₂ is stopped when the GC analyses showed no more conversion of the substrate. The solid is separated by filtration and after double extraction with dichloromethane of resulting solution the main oxidation products benzoic acid and benzoic acid are analyzed by gas chromatography coupled with a mass spectrometer (GC-MS) operating in a selective ion acquisition mode (SIM). Yields are based on the added substrate.

3. Results and Discussion

3.1. Chemical Composition of Purified Bentonite

Table 1 presents the results of chemical analysis of the purified bentonite obtained by the fluorescence X, the analyses of this result indicates that SiO₂ and Al₂O₃ are the main components presents in the sample. The Si/Al ratio of purified bentonite is 2.23, confirms the montmorillonite variety as an almost exclusive component. The number of cations per element mesh of montmorillonite is presented in four third column “Table 1” calculated by following equation (1) [12]:

\[
n_A = \frac{q N V \rho}{100 M_{\text{oxide}}}
\]

Table 1. Chemical compositions of the purified bentonite obtained by fluorescence X.

<table>
<thead>
<tr>
<th>Corresponding oxide</th>
<th>Z</th>
<th>Concentrations</th>
<th>Number of Cation / mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>11</td>
<td>3.98</td>
<td>Na⁺ = 0.454</td>
</tr>
<tr>
<td>MgO</td>
<td>12</td>
<td>3.00</td>
<td>Mg²⁺ = 0.340</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13</td>
<td>22.74</td>
<td>Al³⁺ = 2.587</td>
</tr>
<tr>
<td>SiO₂</td>
<td>14</td>
<td>61.68</td>
<td>Si⁴⁺ = 7.040</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>15</td>
<td>0.072</td>
<td>P⁵⁺ = 0.0079</td>
</tr>
<tr>
<td>SO₃</td>
<td>16</td>
<td>0.181</td>
<td>S²⁻ = 0.0205</td>
</tr>
<tr>
<td>Cl₂O</td>
<td>17</td>
<td>0.282</td>
<td>Cl⁻ = 0.030</td>
</tr>
<tr>
<td>K₂O</td>
<td>19</td>
<td>1.30</td>
<td>K⁺ = 0.147</td>
</tr>
<tr>
<td>CaO</td>
<td>20</td>
<td>0.192</td>
<td>Ca²⁺ = 0.022</td>
</tr>
<tr>
<td>TiO₂</td>
<td>22</td>
<td>0.349</td>
<td>Ti⁴⁺ = 0.039</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>24</td>
<td>1.10</td>
<td>Cr³⁺ = 0.131</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>26</td>
<td>5.175</td>
<td>Fe²⁺ = 0.261</td>
</tr>
<tr>
<td>NiO</td>
<td>28</td>
<td>0.00892</td>
<td>Ni²⁺ = 0.0009</td>
</tr>
</tbody>
</table>

Where M oxide and q are respectively the molar mass and measured fraction of the oxide. N the number of Avogadro, V (485.90, 10-24 cm³) and ρ (2.77 g / cm³) are the volume and density of the elemental montmorillonite. We can deduce the structural formula of the montmorillonite is:

\[
\text{(Si}^{4+}_{7,040}\text{Al}_{0.95}^{3+})\text{ (Al}^{3+}_{2.58}\text{Fe}_{0.26}^{3+}\text{Fe}_{0.26}^{4+})\text{M}_{0.34}^{2+}\text{(Na}_{0.43}\text{K}_{0.14})_{20}\text{O}_{20}\text{(OH)}_{2}
\]

increased from 15.3 Å for purified bentonite up to 19.4 Å for Fe-Al/B, which indicates that the pillaring process is proven successful. This result is better than what is found in the literature [13-15].
<table>
<thead>
<tr>
<th>Samples</th>
<th>$d_{001}$ ($\text{Å}$)</th>
<th>$S_{\text{BET}}$ ($\text{m}^2/\text{g}$)</th>
<th>$S_{\text{ext}}$ ($\text{m}^2/\text{g}$)</th>
<th>$V_p$ ($\text{cm}^3/\text{g}$)</th>
<th>$V_{\mu p}$ ($\text{cm}^3/\text{g}$)</th>
<th>Pore radius ($\text{Å}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>15.3</td>
<td>91.57</td>
<td>67.15</td>
<td>0.106</td>
<td>0.011</td>
<td>15.15</td>
</tr>
<tr>
<td>Fe–Al/B</td>
<td>19.4</td>
<td>229.75</td>
<td>69.01</td>
<td>0.147</td>
<td>0.058</td>
<td>17.87</td>
</tr>
</tbody>
</table>

Abbreviations: $S_{\text{BET}}$: specific surface area; $S_{\text{ext}}$: external surface area; $V_p$: total pore volume at $P/P_0=0.99$; $V_{\mu p}$: micropore volume.

Figure 1. Basal spacing $d_{001}$ of purified bentonite and Fe-Al/B calcined at 500°C.

3.3. Scanning Electron Microscope Analysis (SEM) and the Images of Transmission Electron Microscopy (TEM)

In Figure 2, the scanning electron micrograph (SEM) show for both samples without exception the very small grain size and the total lack of crystal automorphism. Outlines are jagged and usually vague; flakes stick together or are irregularly crumpled “Figure 2”. The most abundant components of bentonites are Si$^{2+}$ and Al$^{3+}$ observed by EDX elemental analysis “Figure 2”, which represents the main components of clay minerals. In the composition of bentonites Na$^+$, Ca$^{2+}$, K$^+$, and Mg$^{2+}$ ions can be observed, these being the interlayer cations between the clay sheets. The absence of titanium ions and the diminution of iron ions from the composition of raw bentonite “Figure 2, a” confirms that the purification process has been achieved “Figure 2, b”. However, the pillared bentonite shows significant changes in the morphology “Figure 2, c” compared with the morphology of the purified bentonite. It can be seen that the Fe-Al/B has become more porous and fluffy, probably due to the change in the surface charge of the particle as a result of pillaring and the reduction in certain amorphous phase originally associated within in purified bentonite. The images of transmission electron microscopy (TEM) of purified bentonite and Fe-Al/B “Figure 3, a, b” exhibit a mixed morphology that contains several well-dispersed montmorillonite platelets parallel-stacked in tactoids. It can be seen too that Fe-Al is successfully well in interlayer of purified bentonite “Figure 3, b”. The results the TEM “Figure 3, b” with value of $d_{001}$ “Table 2” showed that pillarization of Fe-Al in the interlayer of purified bentonite is successfully realized.
3.4. BET Analysis

The specific surface areas (determined by BET method), micropore, surface areas, pore volume and pore radius of the samples are listed in table 2. It can be seen that the specific surface of purified bentonite increased with intercalation of Fe–Al pillars, the Fe–Al/B ($S_{\text{BET}} = 229.75\text{cm}^2/\text{g}$) has a specific surface area almost three times higher than the purified bentonite. This increased of specific surface area is due to the increased distance ($d_{001}$) in agreement with “Table 2” caused the inclining of the surface during the process of intercalation to form pillars. This is likely due to the formation of card house structure that the mesoporous caused, whereas the pillarization process caused new pores that form
micro-porous. As shows in Table 2, the external surface areas and the filling of pores with different sizes tend to an increase with Fe-Al intercalated. So, the total of pore volume is a combination of the volume of microporous with mesoporous volume indicated the pore size distribution in microporous and mesoporous. The particular total pore volume \( (V_p) \) derived from adsorption isotherms increases 0.106, 0.147 \((\text{cm}^3/\text{g})\), respectively, for B and Fe-Al/B, which indicates the porous quality is proportional to the polymeric Fe-Al pillar “Figure 4”, which is exhibit highest specific surface area. As shown in “Figure 4”, nitrogen adsorption/desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distribution of B and Fe-Al/B presented a type IV isotherm with a sharp ramp in the relative pressure on 0.45, which is due to the capillary condensation of nitrogen in the pore. The samples are presented wide, triangular and high-pressure H4 hysteresis loops, which indicate the lamellar structures that confirmed by TEM image “Figure 3”.

3.5. Oxidation of Toluene

3.5.1. Effect of Reaction Time

The partial oxidation of toluene by hydrogen peroxide is performed at 363K and 1 atm with Fe-Al/B catalyst using acetonitrile as solvent. The Figure 5 show the results of the conversion of toluene, the yields and selectivity’s of products as a function of reaction times. The main products of the reaction of oxidation of toluene are benzaldehyde and benzoic acid. It can be observed that the yield of benzaldehyde increases with reaction time within from1h to 6h and then keeps constant, while its selectivity improves with time reached maximum value (69.4%) at 6 h, and then dropped gradually due to the further oxidation of benzaldehyde to benzoic acid. The toluene conversion, the yield and selectivity of benzoic acid increase with time of the reaction “Figure 7”. Again, the yields of the benzaldehyde (27.39%) and benzoic acid (18.57%) reach maxima at 6h, and the conversion of toluene (49.54%) also reaches its maximum simultaneously.
3.5.2. Effect of Catalyst Amount

The effect of the catalyst amount of this reaction is plotted in the Figure 6. It can be seen that in amount range of catalyst from 0.05g to 0.15g, the toluene conversion increases significantly with the increases on the amount of catalyst and the yield of benzaldehyde keeps almost unchanged but the selectivity to benzaldehyde decreases. 0.1g of optimum amount of Fe-Al/B gives 39.34% of toluene conversion, 27.39% yield of benzaldehyde with maximum selectivity of 69.4%. Also noted that significant amounts of benzoic acid is formed without any increase of benzaldehyde when the amount of catalyst is greater of 0.05g with a yield almost 34% at 0.15g, it's because benzoic acid is formed by the oxidation of benzaldehyd. Moreover, from figure 6 is observed that the toluene conversion and the yields of benzaldehyde a benzoic acid decrease falls with further increase of catalyst. It is known that the phenomena of activity decrease in the high catalyst amount can be explained as the so-called catalyst inhibitor conversion.
3.5.3. Effect of Peroxide Concentration

The influence of toluene to amount of hydrogen peroxide is given in Figure 7. It can be observed that the increase in the amount of hydrogen peroxide increases the conversion of toluene and benzaldehyde selectivity. However, after an optimum amount of oxidant, the activity falls. The maximum conversion of toluene to benzaldehyde is observed at 10 ml of peroxide. The increase of oxidant causes further oxidation of benzaldehyde of benzoic acid. However, when too much amount of oxidant (volume > 10 ml) is added to the reaction, the reaction mixture doesn't become homogeneous at 363K, which resulted in the slowed of conversion of toluene. Indeed, the consumption of hydrogen peroxide is caused competitively by its self-decomposition and the oxidation of toluene.

3.5.4. Effect of Solvent

The choice of the solvent is an essential requisite for any reaction. The results of activity in both solvents of varying polarity are tabulated in Table 3. From the table, it can be deduced that the reaction proceeds with great vigor in acetonitrile compared to acetic acid. In the literature [16], have suggested that in an organic solvent, because of the higher reactivity of organic compounds toward hydroxyl radical in comparison with the reactivity of H$_2$O$_2$, chain processes of hydrogen peroxide decomposition will be accompanied with conjugated solvent oxidation reactions because solvent molecules usually react with hydroxyl...
radicals. However, acetonitrile is used as solvent with hydrogen peroxide as oxidant in our system has terrible effect on the selectivity of benzaldehyde and benzoic acid but, acetic acid is seems that not the key factor in the formation of benzaldehyde.

Table 3. Effect of solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>Benzaldehyde</th>
<th>Benzoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Yield (%)</td>
<td>Selectivity (%)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>49.54</td>
<td>27.39</td>
<td>69.40</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>10.34</td>
<td>9.42</td>
<td>40.56</td>
</tr>
</tbody>
</table>

Conditions: Toluene: solvent: H₂O₂: water, 1.5 ml: 12 ml: 10ml: 10 ml, catalyst, 0.1 g; T=363K, time, 6h.

4. Conclusions

The results of the Liquid phase oxidation of toluene with hydrogen peroxide as oxidant show that Fe-Al/B pillared clay prepared here in is catalytically highly efficient catalyst in this reaction. The Physicochemical characterization of purified bentonite and Fe-Al/B catalyst with XRD, BET, SEM and TEM techniques showed that they are porous materials with the successfully pillarization of mixed polyhydroxo complexes of iron and aluminum in the interlayer. The Fe-Al/B pillared clay possess significant activity for the oxidation of toluene, the optimal conditions are determined at 363K and 1 atm, namely the reaction time of 6h, in 1.5 ml of toluene, the catalyst concentration at 0.1g, the volume ratio of acetonitrile: water: hydrogen peroxide is 12:10:10. In this condition, Fe-Al/B shows the high selectivity of benzaldehyde of 69.4% with 39.34% of toluene conversion.

References


