Synthesis and characterization of fly ash supported sulfated zirconia catalyst for benzylation reactions

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ABSTRACT

Synthesis of highly active nano-crystalline, thermally stabilized solid acid catalyst has been reported by loading different weight fractions of sulfated zirconia on chemically activated fly ash through two step solgel technique. The catalysts were characterized using powder XRD, FT-IR, N2-adsorption desorption study, CHNS elemental analysis, SEM-EDAX and their acidity were measured by pyridine adsorbed FTIR. Liquid phase benzylation of benzene and toluene with benzyl chloride was studied as test reaction for catalytic activity of SZF catalysts. A very high conversion of benzene (87%) and toluene (93%) were observed, which is attributed to significant amount of acid site on the catalyst surface. The FTIR study of the pyridine adsorbed samples reflects the presence of Brønsted as well as Lewis acid sites. The catalyst with 12 wt.% zirconia (SZF-12) was regenerated and reused up to four reaction cycles with equal efficiency as in the first run.

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1. Introduction

Fly ash a by-product recovered from coal based electric power plants [1], is the finest coal combustion residue (0.2–90 μm) with a specific surface area, typically between 250 and 600 m²/kg [1]. Chemically fly ash is an ensemble of compounds such as silica, alumina, ferric oxide, calcium oxide and other metal oxides such as Mn2O3 and TiO2 [2] with inert crystallised phases such as mullite, quartz and magnetite [3]. Porous spherical aluminosilicate particles, which are referred to as ash microspheres, aluminosilicate microspheres, or cenospheres, are among the most valuable fly ash components [4]. Main applications of fly ash are in the field of cement and other construction materials [5], agriculture, metal recovery, water and atmospheric pollution control [6] etc. Nevertheless important advances in the applications of fly ash are its catalytic role in oxidation [7], chlorination [8], synthesis of 2-mercaptobenzothiazole derivatives under microwave irradiation [9] and as solid acid catalyst for esterification reactions, for the synthesis of aspirin and oil of wintergreen [10].

Zirconia, a versatile material besides being used in structural ceramics and electronic ceramic products [11] is well reported as solid acid due to high acidity induced by sulfation [12]. Several industrially important reactions such as isomerization, Friedel Crafts acylation, alkylation, esterification [13] etc. were catalyzed by sulfated zirconia due to its high acidity. Silica supported sulfated zirconia were synthesized by grafting sulfated zirconia on the surface of a silica aerogel to generate relatively strong Brønsted and Lewis acid sites on the surface to catalyze n-hexane isomerization reactions [14]. As received fly ash (silica 58%) was chemically activated to increase silica up to 80% and was thought to be used for supporting sulfated zirconia. The use of fly ash as support not only reduced the cost of the catalyst it also showed high acidity and catalytic activity for benzylation of benzene and toluene. The product diphenylmethane and its derivatives are widely used as pharmaceuticals, petrochemicals, cosmetics, dyes, fine chemicals, insulators etc [15]. Previously, several heterogeneous catalysts such as Fe containing mesoporous silicate catalysts [16], clay (K-10, montmorillonite), H-beta, MFI structured titanosilicate (TS-1) and heteropoly acids [HPA, namely dodeca-tungstophosphoric acid [H₃PO₄·12WO₃·xH₂O] supported on clay, H-beta and TS-1 [17], sulfated zirconia [18] and metal modified zeolites [19] were used effectively for Friedel-Crafts alkylations. The synthesized SZF catalysts gives a solution to overcome the use of harmful liquid acids and other costly commercial heterogeneous catalysts for industrially important benzylation reaction.

2. Experimental

2.1. Materials

Fly ash [Class F type (SiO₂ + Al₂O₃ >70%)] produced from combustion of bituminous coal, collected from Kota Thermal Power Plant (Rajasthan, India) was used as solid support after acid activation. The components of fly ash are SiO₂ (54%), Al₂O₃ (21%), Fe₂O₃ (9%), CaO (1.6%), MgO (0.8%), TiO₂ (1.3%), Na₂O (4.8%), K₂O (3.2%) and
trace elements (4.0%). The L.O.I (loss on ignition) was 3 wt.% at 900 °C for 4 h. Zirconium propoxide (70 wt.%) was procured from Sigma Aldrich, while concentrated H2SO4 (98%), n-Propanol (99.99%), benzene (99.8%), toluene (99.8%) and benzyl chloride (99%) were purchased from s. d. fine Chem. Ltd., India and were used as such.

2.2. Catalyst preparation

The fly ash-sulfated zirconia catalysts (SZF-6, SZF-9 and SZF-12) were prepared by loading zirconia 6, 9 and 12 wt.% on activated fly ash by two step sol-gel technique.

The activation of fly ash was performed in a stirred reactor taking fly ash and concentrated H2SO4 acid in the ratio of 1:2 followed by drying at 110 °C and calcination at 450 °C for 4 h similar to our previous work [10]. Zirconium propoxide (1.08 g for 6 wt.%, 1.62 g for 9 wt.% and 2.16 g for 12 wt.%) diluted with 15 ml n-propanol was taken in glass beaker. The 5 g activated fly ash preheated at 400 °C for 4 h was added into it under constant stirring. Water was added drop wise in this stirred mixture (water: zirconium propoxide molar ratio = 4:1) for hydrolysis and polycondensation. The gel thus formed was aged for 24 h followed by drying at 110 °C for 24 h to remove the solvent from the pores of the gel. In the second step, the dried gel was powdered and sulfated with concentrated H2SO4 solution (15 ml 1 N H2SO4 solution/1 gm powdered dried gel) under stirring for 1 h. The sulfated gel was filtered and dried at 110 °C for 24 h followed by calcination at 550 °C for 2 h in a muffle furnace under static condition.

2.3. Catalyst characterization

X-ray diffraction pattern were recorded on diffractometer (Philips XPert) using CuKα radiation (λ = 1.54056 Å), angle range was between 0 and 80° at a scanning rate of 0.04° s⁻¹. Crystallite size of the crystalline phase was determined from the peak of maximum intensity (2θ = 26.57) by using Scherrer formula [20] as Eq. (1) with a shape factor (K) of 0.9.

\[
\text{Crystallite size} = \frac{K \lambda}{W \cos \theta}
\]

where, \(W = W_0 - W_c\); \(W_0\) is the broadened profile width of experimental sample and \(W_c\) is the standard profile width of reference silicon sample.

The FT-IR study of the samples was done by FT-IR spectrophotometer (IRPrestige-21, Shimadzu) in DRS (Diffuse Reflectance Spectroscopy) system by mixing the sample with KBr in 1:20 weight ratio. The Brunsted and Lewis acidity of the catalysts were measured by pyridine adsorbed FT-IR. The sample (0.2 g) was activated at 450 °C for 2 h and was exposed to pyridine (25 ml) for 24 h. The spectra of the samples were recorded in the range of 400–4000 cm⁻¹ at room temperature. Specific surface area, pore volume and pore size in the samples were determined from \(N_2\) adsorption–desorption isotherms at 77 K by NOVA 1000e Surface Area and Pore Size Analyzer using BET and BJH approaches [21]. The sample was degassed under vacuum at 120 °C for 4 h, prior to adsorption measurement to evacuate the physisorbed moisture and the isotherm was recorded with 20 points adsorption and desorption. The sulfur content was analyzed using CHNS/O elemental analyzer (Perkin-Elmer, 2400). The detailed imaging information about the morphology and surface texture of the catalyst was provided by SEM (Philips XL30 ESEM TMP).

2.4. Catalytic activity of (SZF) catalysts

The benzylation of benzene and toluene with benzyl chloride in solvent free liquid phase reaction was carried by SZF catalyst as shown in Scheme 1.

\[
\text{SZF-12} \xrightarrow{\text{Benzyl chloride}} \text{Benzyldihydrine}\]

Scheme 1. Benzylation of benzene and toluene with benzyl chloride over SZF-12 catalyst.

The benzylation was performed in liquid phase batch reactor consisting of 25 ml round bottom flask with condenser in a constant temperature oil bath with magnetic stirring. A mixture of benzene (0.78 g, 20 mmol) or toluene (0.94 g, 10 mmol) and benzyl chloride (1.1 g, 10 mmol) was taken in round bottom flask. The catalyst (substrate to catalyst ratio = 10), activated at 450 °C for 2 h was added in the reaction mixture. The reaction mixture was kept on hot oil at different temperatures ranging from 60 to 120 °C and time from 30 min to 8 h. The reactions were carried out at different molar ratio of substrate (benzene or toluene) and benzyl chloride and at different temperatures in the range of 60 to 120 °C for time ranging from 30 min to 24 h. The kinetics of benzylation reaction was studied using SZF-12 as it showed highest catalytic activity. After completion of the reaction the catalyst was filtered and the reaction mixture was analyzed by Gas Chromatography (Dani Master GC) having a flame ionization detector and HP-5 capillary column of 30 m length and 0.25 mm diameter, programmed oven temperature of 50–280 °C and \(N_2\) (1.5 ml/min) as a carrier gas. The conversion of benzene or toluene was calculated by using weight percent method [10].

2.5. Catalyst regeneration

The used catalyst (SZF-12) was washed with acetone dried in oven at 110 °C for 12 h followed by activation at 450 °C for 2 h and reused for next reaction cycle under similar reaction conditions as earlier.

3. Results and discussion

3.1. Catalyst characterization

The physicochemical properties of the fly ash before and after chemical activation and after loading Sulfated-Zirconia are summarized in Table 1. The silica content in chemically activated fly ash (CFA) is greatly increased from 54 to 80%. The silica content of as received fly ash was analyzed by Atomic Absorption Spectrophotometer while increased silica after chemical activation is evident from SEM-EDAX spectra in Fig. 1. The increase in silica content after chemical activation is due to the loss of significant amount of other components during the H2SO4 treatment.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Silica (wt.%)</th>
<th>Crystallite size (nm)</th>
<th>Sulfur (wt.%)</th>
<th>BET surface area (m²/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>54</td>
<td>33</td>
<td>0.3</td>
<td>8</td>
<td>29</td>
</tr>
<tr>
<td>CFA</td>
<td>80</td>
<td>12</td>
<td>1.0</td>
<td>10</td>
<td>26</td>
</tr>
<tr>
<td>SZF-6</td>
<td>80</td>
<td>11</td>
<td>2.4</td>
<td>7</td>
<td>37</td>
</tr>
<tr>
<td>SZF-9</td>
<td>80</td>
<td>9</td>
<td>3.6</td>
<td>6</td>
<td>43</td>
</tr>
<tr>
<td>SZF-12</td>
<td>80</td>
<td>7</td>
<td>5.6</td>
<td>4</td>
<td>51</td>
</tr>
</tbody>
</table>
X-ray diffraction pattern of activated fly ash (CFA) in Fig. 2 (a) shows increased amorphous content with crystallite size 12 nm [10]. The XRD patterns of the catalysts SZF-6, SZF-9 and SZF-12 as illustrated in Fig. 2 (b) shows a broad peak at around 22°(2θ) indicating the presence of amorphous form of zirconia which is formed due to the incorporation of zirconium atoms in the framework of amorphous SiO₂ of fly ash [22,23] to form zircon (ZrSiO₄) as the major component [11]. The peaks at 50°, 60° and a little sharp peak at 78° 2θ showed the presence of tetragonal phase of zirconia [23], which increases with increase in ZrO₂ content from 6 to 12 wt.%, while a broad peak at 22° (20) represents monoclinic phase in all the catalysts. The crystallite size of SZF-6 containing 6 wt.% zirconia is 11 nm, which decreases to 9 and 7 nm respectively for SZF-9 and SZF-12 with increasing zirconia content from 9 to 12 wt.% as presented in Table 1. The absence of large sharp lines in ZrO₂ rich SZF-12 indicates that zirconia crystallites in this catalyst are either too small to be detected by XRD or they are dispersed through the fly ash network in small amount.

The FT-IR spectrum of fly ash, before and after chemical activation Fig. 3, shows a broad band between 3400 and 3000 cm⁻¹, which is attributed to surface –OH groups of –Si–OH and adsorbed water.
molecules on the surface. The broadness of the band is due to the strong hydrogen bonding [10]. The hydroxyl groups do not exist in isolation and a high degree of association is experienced as a result of extensive hydrogen bonding with other hydroxyl groups. A peak at 1650 cm$^{-1}$ in the spectra of both the samples is attributed to bending mode (δO–H) of water molecule. The FT-IR spectrum of SZF catalysts is shown in Fig. 4 (a) shows –OH peaks characteristics of SiO$_2$ of fly ash and incorporated ZrO$_2$. The SZF catalysts show shifting of band at 1095 cm$^{-1}$ towards lower wave number (954 cm$^{-1}$) with highest peak intensity for SZF-12 due to the formation of Zr–O–Si linkages [24,25]. However, the ZrO$_2$ was also observed to be present as dispersed clusters on SiO$_2$ of fly ash, as is evident from the characteristic peak of zirconia at 440 and 525 cm$^{-1}$ [26]. The FT-IR spectra of SZF catalysts in Fig. 4 (b) shows the bands for sulfate group between 1400 and 1040 cm$^{-1}$ (1400, 1156, 1040 and 1000 cm$^{-1}$), for asymmetric and symmetric stretching vibrations of S=O double bond, partially ionized S=O double bond and S–O single bonds [27]. The bands at ~1040 are attributed to the asymmetric stretching mode of vibrations of S–O bonds. The S=O bond is characterized by the band at ~1400 cm$^{-1}$, which is attributed to asymmetric stretching vibration of S=O bond. However, in hydrated SZF catalyst, the sulfate is bonded with water molecule by hydrogen bonding and therefore, S=O bond is partially ionized and does not show the band at ~1400 cm$^{-1}$ which is similar as observed in sulfated zirconia [27]. The intensity of these bands is very high in SZF-12 which is due to increased zirconia (12 wt.%) and sulfur (5.6 wt.%) content.

The FT-IR spectra, obtained after pyridine adsorption on SZF-6, SZF-9 and SZF-12 catalysts, are presented in Fig. 4 (c), which shows bands in range of 1400–650 cm$^{-1}$ for adsorbed pyridine at Brønsted and Lewis sites. Two diagnostic peaks characteristic of Brønsted and Lewis sites were observed at 1554 cm$^{-1}$ and 1450 cm$^{-1}$ respectively. The spectra of pyridine adsorbed on SZF-12 showed an intense peak at 1554 and 1445 cm$^{-1}$ showing the presence of higher amount of Brønsted and Lewis acidity in SZF-12 as compared to SZF-6 and SZF-9 which is attributed to increase in zirconia content from 6 to 12 wt.%, which enhances the loading of sulfur responsible for increase in concentration of Brønsted and Lewis acid sites [28].

An increase in zirconia loading from 6 to 12 wt.% is seen to increase in agglomeration thus decreasing the surface area as evident from Figs. 7–9. The addition of zirconia is reported to increase density of fly ash [29], which is also reflected from SEM micrograph. The surface area of as received and activated fly ash were calculated to be 8 m$^2$/g from respectively as given in Table 1. The chemical activation of fly ash results to higher surface area which increases the probability of ZrO$_2$ loading. Isotherms shown in Fig. 9 are of type IV, which are characteristics of mesoporous materials showing the catalysts are mesoporous. The presence of large mesopores is also confirmed by their low surface area (4–7 m$^2$/g) and higher pore size.
(37–51 cm³/g). The inflection point in the N₂ adsorption isotherms in the samples is not sharp, indicating that the pores are not of uniform size and have broad distribution. The isotherms possess a broad hysteresis of type H₃, reflecting the presence of large mesopores. A progressive decrease in surface area and decrease in pore diameter is observed with increasing zirconia and sulfur content in SZF catalyst. The decrease of BET surface area was related to the blockage of the smallest pores induced by sulfation. It seems that increase in the amount of zirconia and sulfate groups contribute to the blockage of mesopores of smallest aperture making them inaccessible of the N₂ molecule [30]. This phenomenon is accompanied by the decrease in BET surface area and pore volume. Almost similar evaluation of the BET surface area and pore volume was also observed earlier for Sulfur/ZrN₀.6 in silica supported zirconia catalyst and this behavior was produced due to gelation mechanism leading to solids with enhanced pore diameter and reduced small mesopores [30].

The increase in sulfur in activated fly ash from 0.3 to 1.0 wt.% is due to use of sulfuric acid for chemical activation. After zirconia incorporation and sulfation the total sulfur content in the catalysts increases from 2 to 5.6% Table 1. The sulfur in the SZF catalyst is bonded with zirconia as covalent and ionic bonds are responsible for the increased acidity in the catalysts. There was no significant acidity in activated fly ash (CFA) but after loading zirconia acidity increases due to enhanced sulfation.

3.2. Proposed model structure for SZF catalyst

The proposed model structure of SZF is shown in Scheme 2(a) and (b). The zirconia clusters are supported on fly ash surface by Si–O–Zr linkages and sulfate species are bonded with zirconia surface. The sulfate species are bonded with zirconium atom as bidentate chelating.
The catalytic activity of SZF catalysts for benzylation reactions is influenced by the molar ratio of benzene to benzyl chloride and reaction temperature. The catalyst SZF-12, containing 12 wt% zirconia and 5.6 wt% sulfur, showed the highest catalytic activity in the benzyl chloride reaction at 80 °C and 110 °C for 4 h. For benzene and toluene, the conversions were 87% and 93%, respectively. The selectivity of diphenylmethane and p-benzyl toluene was 100% at 80 °C, whereas the yield of diphenylmethane and p-benzyl toluene was 68% and 72%, respectively, at 90 °C and 100 °C.

### Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%) of Benzene</th>
<th>Selectivity (%) of Diphenylmethane</th>
<th>Conversion (%) of Toluene</th>
<th>Selectivity (%) of p-Benzyl Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>CFA</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>SZF-6</td>
<td>47</td>
<td>100</td>
<td>56</td>
<td>99</td>
</tr>
<tr>
<td>SZF-9</td>
<td>72</td>
<td>100</td>
<td>79</td>
<td>99</td>
</tr>
<tr>
<td>SZF-12</td>
<td>87</td>
<td>100</td>
<td>93</td>
<td>99</td>
</tr>
</tbody>
</table>

Reaction condition: * Temperature = 80 °C; Time = 4 h; Molar ratio (benzene/benzyl chloride) 1:1; substrate/catalyst ratio = 10. * Temperature = 110 °C; Time = 4 h; Molar ratio (toluene/benzyl chloride) 1:1; substrate/catalyst ratio = 10.

The optimized reaction time required to achieve maximum conversion was carried out at 80 and 110 °C for different time intervals ranging from 30 min to 8 h. The conversion of benzene and toluene was gradually increased with time giving maximum efficiency at 87% and 93% respectively after 4 h which remained constant till 8 h. The effect of the molar ratio of benzene to benzyl chloride and toluene to benzyl chloride was studied at a reaction temperature 80 and 110 °C for 4 h. At the molar ratio of 1:1 maximum conversion of benzene and toluene was 93% at 110 °C with 99% selectivity of p-benzyl toluene, selectivity was decreased with further increase in temperature which is assigned to the formation of other di or tri benzylated products of benzene and toluene at higher temperatures.

#### 3.3.2. Effect of reaction time

The optimization of reaction time required to achieve maximum conversion was carried out at 80 and 110 °C for different time intervals ranging from 30 min to 8 h. The conversion of benzene and toluene was gradually increased with time giving maximum efficiency at 87% and 93% respectively after 4 h which remained constant till 8 h.

#### 3.3.3. Effect of molar ratio (substrate/benzyl chloride)

The effect of the molar ratio of benzene to benzyl chloride and toluene to benzyl chloride was studied at a reaction temperature 80 and 110 °C for 4 h. At the molar ratio of 1:1 maximum conversion of benzene and toluene with highest selectivity of their respective products were obtained (Table 3). With increasing the molar ratio of benzene or toluene with benzyl chloride, the conversion as well as selectivity of diphenylmethane (DPM) and p-benzyl toluene was observed to be decreased which is attributed to formation of di or tri alkylated products by alkylation reaction of benzylated substrates with excess benzyl chloride.

#### 3.3.4. Mechanism

The surface acid sites (Brønsted and Lewis) of the catalyst produce carbocations from benzyl chloride as shown in Scheme 3, which attack on the aromatic substrate and form benzylated product by simple electrophilic substitution reaction. The higher conversion of toluene as compared to benzene shows higher reactivity of toluene for benzylation. This is assigned to presence of electron donating methyl group on aromatic nucleus of toluene, which activates the aromatic ring for electrophilic substitution reaction.

#### 3.4. Regeneration study

The used SZF-12 catalyst from both the reaction mixtures (benzylation of benzene and toluene) were filtered, washed with acetone and...
regenerated by heating at 450 °C for 2 h. The regenerated catalysts were used for the next reaction cycles under similar reaction conditions to first cycle. The catalyst was found efficient up to 4 cycles giving conversion in the range of 87–82%. The catalyst was easily regenerated by thermal treatment without loss of catalytic activity. The FT-IR spectra of regenerated catalyst after second cycle in Fig. 10 shows similarity with that of fresh catalyst indicating no change in chemical composition of catalyst surface. The significant decrease in conversion after fourth cycle is due to the deposition of carbonaceous material on the external surface of the used catalyst that may block the active sites present on the catalyst.

4. Conclusion

The study provides fly ash supported sulfated zirconia as an efficient solid acid catalyst possessing significant amount of acidity. The chemical activation of fly ash by acid leaching results in increased silica content and thus surface hydroxyl contents, which are responsible for efficient loading of zirconia on fly ash support. In SZF catalysts zirconia reacts with silica of fly ash and form Si–O–Zr phase which increases with increase in zirconia content in the catalyst. The catalyst SZF-12 exhibit high acidity due to high zirconia (12 wt.%) and sulfur (5.6 wt.%) content bonded with zirconia generating Brønsted and Lewis acid sites responsible for higher conversion of benzene and toluene. The catalyst is also recyclable suggesting that acid sites of the catalysts are not lixiviated during the reaction. The novelty of the work is that fly ash can replace pure silica after its suitable activation as a solid support for loading of zirconia. The fly ash supported catalysts are cost effective, atom efficient and thus finds a novel route to utilize abundant waste fly ash.

Table 3
Conversion (%) of benzene and toluene with SZF-12 catalyst at different molar ratios of benzene and toluene with benzyl chloride.

<table>
<thead>
<tr>
<th>Molar ratio (benzene or toluene/benzyl chloride)</th>
<th>Conversion % of benzene</th>
<th>Selectivity % of diphenyl-methane</th>
<th>Selectivity % of other isomers</th>
<th>Conversion % of toluene</th>
<th>Selectivity % of p-benzyl toluene</th>
<th>Selectivity % of other isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>87</td>
<td>100</td>
<td>Nil</td>
<td>93</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>1:2</td>
<td>78</td>
<td>81</td>
<td>19</td>
<td>82</td>
<td>71</td>
<td>29</td>
</tr>
<tr>
<td>1:4</td>
<td>65</td>
<td>74</td>
<td>26</td>
<td>70</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

Reaction condition: aTemperature = 80 °C; Time = 4 h; substrate/catalyst ratio = 10. bTemperature = 110 °C; Time = 4 h; substrate/catalyst ratio = 10.
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