Liquid phase benzylolation over iron incorporated sulphated zirconia systems

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Received 31 December 2002; revised 14 September 2005

The utility of iron incorporated sulphated zirconia for benzylolation reaction has been studied. Physico-chemical characterization of the prepared systems have been achieved using data on XRD, laser Raman spectra, IR spectra, surface area, pore volume, EDX and acidity. Incorporation of iron improves the surface properties of sulphated zirconia. Surface area and acidity is enhanced and tetragonal phase is stabilized with no trace of monoclinic phase. All the systems show high catalytic activity and selectivity for monoalkylation.

IPC Code: Int. Cl. 7 B01J21/00; C07B37/000

Friedel-Crafts alkylation forms the major route for the introduction of alkyl side chains into aromatic ring. The alkylation of aromatic compounds containing electron donating groups (–OH, alkyl or alkoxy) can be easily accomplished while it is difficult in the absence of an activating group. A wide range of solid acid catalysts from clays1 and zeolites2–6 to heteropoly acids7–9 has been widely tested for their applicability towards this reaction. Several reports are available regarding the utility of sulphated oxides for Friedel Crafts reactions8–10. Clark et al.8, Clark et al.8, Clark et al.8, Clark et al.8, Clark et al.8, Clark et al.8, Clark et al.8, Clark et al.8, Clark et al.8 investigated the use of sulphated zirconia as catalysts for the alkylation of benzene with long chain linear alkenes to form linear alkyl benzenes, Samantaray et al.11 have studied the physico-chemical properties and catalytic activity of sulphated titania for the gas phase alkylation of benzene and substituted benzenes using iso-propanol as alkylation agent.

In continuation with our work on properties and catalytic activity of modified zirconia systems12,13, we report herein a detailed study of the liquid phase benzylolation of benzene using benzy l chloride as alkylation agent over iron promoted sulphated zirconia systems. A process optimization has also been undertaken.

Materials and Methods

Iron incorporated sulphated zirconia systems were prepared by a single step impregnation of hydrous zirconium oxide with 1N H₂SO₄ (10 ml/g) and ferric nitrate solution. The iron loading was varied from 2 to 10% as indicated in the parenthesis during sample notation. The samples after overnight drying at 120°C were calcined at 700°C for three hours.

Characterization of the samples was carried out by BET surface area and pore volume measurements (Micromeritics Gemini Surface Area Analyzer), XRD (Rigaku D-max C X-Ray Diffractometer), TG (Shimadzu TGA-50), IR (Shimadzu DR 8001) and laser Raman spectroscopy (Dilor Jobin spectrophotometer). The surface acidity measurements were carried out by ammonia TPD and perylene adsorption studies. The sulphate content in the sample was estimated by EDX analysis (stereoean 440).

For benzylolation reaction, the aromatic substrate and the benzylating agent in the required molar ratio were taken in a 50 ml R.B flask containing 0.1 g of the catalyst. The mixture was magnetically stirred at the desired temperature, maintained using an oil bath. The influence of reaction parameters like substrate: benzylating agent molar ratio, reaction temperature, etc. were investigated in detail. The reusability of the catalyst and metal leaching were also tested for understanding the molecular aspects of the reaction. The product analysis was done using a Chemito 8610 gas chromatograph equipped with a flame ionization detector and SE-30 column.

Results and Discussion

Table 1 presents a comparative evaluation of the physico chemical properties of different catalyst
Table 1—A comparative evaluation of the physico-chemical properties

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>Sulphate content (wt %)</th>
<th>Sulphate retained (%)</th>
<th>Total acidity (NH₃ desorbed, mmol/g)</th>
<th>Perylene adsorbed (10⁻⁶ mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>32.7</td>
<td>0.065</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
<td>0.09</td>
</tr>
<tr>
<td>SZ</td>
<td>44.8</td>
<td>0.079</td>
<td>18.5</td>
<td>47.6</td>
<td>1.05</td>
<td>2.75</td>
</tr>
<tr>
<td>Fe(2)SZ</td>
<td>61.1</td>
<td>0.082</td>
<td>30.1</td>
<td>84.7</td>
<td>1.23</td>
<td>3.67</td>
</tr>
<tr>
<td>Fe(4)SZ</td>
<td>60.4</td>
<td>0.083</td>
<td>28.9</td>
<td>81.3</td>
<td>1.24</td>
<td>4.18</td>
</tr>
<tr>
<td>Fe(6)SZ</td>
<td>59.6</td>
<td>0.085</td>
<td>27.1</td>
<td>76.4</td>
<td>1.26</td>
<td>7.37</td>
</tr>
<tr>
<td>Fe(8)SZ</td>
<td>57.3</td>
<td>0.075</td>
<td>24.7</td>
<td>69.4</td>
<td>1.26</td>
<td>8.85</td>
</tr>
<tr>
<td>Fe(10)SZ</td>
<td>55.7</td>
<td>0.088</td>
<td>23.1</td>
<td>64.9</td>
<td>1.30</td>
<td>10.69</td>
</tr>
</tbody>
</table>

systems. Sulphation and iron incorporation resulted in an enhancement in surface area, which may be attributed to the inhibition of crystallization and particle growth. A slight lowering of surface area values with increasing iron loading may be a consequence of the partial agglomeration of iron particles.

XRD patterns (Fig. 1) show considerable stabilization of catalytically active tetragonal phase after sulphation. The bulk structure of SZ remains virtually unchanged by the incorporation of iron except for a lowering in crystallinity. Lowering of crystallinity becomes prominent at high iron loadings. At high iron loadings monoclinic phase disappears completely. Laser Raman spectra (Fig. 2) supplements XRD results. The appearance of Fe₂O₃ peaks (224, 300 and 409 cm⁻¹) in the laser Raman spectrum and its absence in XRD confirms the presence of iron in highly dispersed form on the catalyst surface even at high loadings. Peaks due to sulphate species could be located in the laser as well.
peaks due to S-O and S=O stretching modes of surface sulphate species show up around 1059 and 1319 cm\(^{-1}\) respectively in the laser Raman spectrum\(^{12}\). However, distinct characterization of coordination becomes difficult due to the broadness of the spectrum. The broad peak around 1059 cm\(^{-1}\) in the IR spectrum (Fig. 3) represents the S-O mode of vibration of a chelating bidentate sulphate ion coordinated to a metal cation\(^{11}\). The band around 1375 cm\(^{-1}\) arises from highly covalent character of the S=O of isolated sulphate species on a highly dehydrated oxide surface\(^{13,16}\). No considerable difference could be detected in the spectrum of simple sulphated and iron loaded systems. TG analysis confirms the thermal stability of the systems.

Incorporation of iron significantly improves the sulphate retaining ability as observed from EDX data (Table 1). The sulphate content higher than that required for monolayer coverage implies the migration of the sulphate moieties into the bulk\(^{17}\). The bulk species may be retained to a greater extent when compared to the surface species during high temperature calcination. A slight lowering of sulphate content was observed at high iron loadings. It may be assumed that dispersion of iron particles restricts the sulphate species more or less to the surface, minimizing their migration into the bulk which facilitates their easy removal during high temperature calcination.

Figure 4 illustrates the acid strength distribution of iron doped sulphated zirconia systems. Incorporation of iron and sulphate species greatly enhances the surface acidity. The total acidities of simple sulphated and iron incorporated systems are almost comparable. However, there is a marked difference in the acid strength distribution. An increase in iron loading produced a considerable increase in the amount of strong acid sites at the expense of weak acid sites. Perylene adsorption studies provide an general idea regarding the Lewis acidity of the systems in presence of Bronsted acidity\(^{8,19}\). Modification results in considerable enhancement in the Lewis acidity of zirconia; Lewis acidity increases with increasing iron content (Table 1). A detailed account of the physicochemical characterization has been reported earlier\(^{20}\).

**Catalytic activity studies**

Catalytic activity of the prepared systems was tested for benzylation of aromatics using benzyl chloride. Iron incorporated systems exhibit very high reactivity for the benzylation of benzene with benzyl chloride as revealed from Table 2. An increase in iron content seems beneficial for the reaction. The percentage conversion increases gradually with an increase in iron loading and leveled off after an iron content of 8%. Increase in iron content, however, produces a negative impact on selectivity; the selectivity to diphenylmethane undergoes a drastic reduction from 97.5 to 71.1%. The increase in percentage conversion is rather marginal when compared to the decrease in selectivity.

The catalytic activity of the iron promoted systems may be correlated with the Lewis acidity. The increase in Lewis acidity was rather sharp when the
The reaction temperature plays a major role in deciding the catalytic activity and selectivity. Influence of reaction temperature was screened using toluene. At low temperatures, percentage conversion was very low. An increase in temperature results in enhanced activity. An interesting observation was the sharp rise in conversion obtained when the temperature was varied in the narrow range of 10°C from 60°C to 70°C. A further increase in temperature had only a minor influence on the percentage conversion. Temperature also had a marked influence on selectivity. At low temperatures, 100% selectivity to the monoalkylated products was obtained. An increase in reaction temperature results in a lowering of selectivity.

Influence of reaction time

The progress of the reaction with time was monitored in the case of benzylaion of toluene 70°C with benzyl chloride. An induction period was observed in the beginning of the case of iron-doped systems whereas a gradual rise in conversion was observed with simple SZ system. After the first 30 minutes, the reaction was almost rapidly driven to completion when Fe(2) system was employed. In the case of Fe(10)SZ, the reaction was completed within 15 minutes even at 70°C. The induction period is considerably shortened at high iron loadings.

Influence of molar ratio

The variation in the catalytic activity with toluene to benzyl chloride molar ratio was also examined for Fe(2)SZ and Fe(10)SZ systems. Increase in toluene to benzyl chloride molar ratio resulted in lowering of the percentage conversion in the case of Fe(2)SZ system. However, the molar ratio had little effect on the catalytic activity at higher iron loadings and in the case of Fe(10)SZ, complete conversion was obtained irrespective of the molar ratio selected. The negative influence of higher toluene to benzyl chloride molar ratios may be explained on the basis of the dilution effect at high solvent levels.

Irrespective of the catalyst composition, the product selectivity depends on the molar ratio. At higher toluene to benzyl chloride ratios, the amount of dialkylation was negligible while it considerably increased at low molar ratios. This may be rationalised on the basis of the relative concentration of benzyl chloride molecules. At low toluene to benzyl chloride ratios, high concentrations of benzyl chloride species in the reaction mixture favour successive alkylation.

Influence of calcination temperature

The influence of calcination temperature on the catalytic activity for the benzylaion of benzene was
tested. An increase in the calcination temperature resulted in a progressive increase in the catalytic activity. A temperature of 700°C was found to be the optimum temperature for calcination. For monoalkylated products, 100% selectivity was observed at low calcination temperatures. For higher calcination temperatures, conversion increased at the expense of selectivity. The progressive increase in the percentage conversion with calcination temperature correlates with increase in Lewis acidity obtained by perylene adsorption studies. After 600°C, the increase was rather sharp, which suggests that the crystalline nature of the catalyst may also be contributing to the activity. Tetragonal phase formation starts at around 600°C.

Reusability of catalyst systems

The reusability of the systems for the benzylolation reaction was investigated. Gradual drop was observed in the percentage conversion [from 91.7 to 65.2% for Fe(2)SZ and 98.5 to 79.6% for Fe(10)SZ] as the catalyst was subjected to regeneration. However, even after five successive recycling operations, satisfactory yields could be obtained. The XRD patterns of the used catalyst systems confirm the retention of crystalline nature in Fe(2)SZ system, except for a slight lowering of intensity. Recycling operations resulted in the appearance of traces of monoclinic phase in Fe(10)SZ system, which was absent in the fresh sample.

Metal leaching

The alteration in the crystalline structure observed in the XRD pattern at high iron loadings led us to some investigations on the chemical changes involved in the catalyst during recycling. In order to test for metal leaching, the reaction was continued for half an hour after filtering off the catalyst. A slight enhancement in the percentage conversion was monitored suggesting the partially homogeneous nature of the reaction. The increase in the conversion after filtering off the catalyst is more prominent for the high loaded iron system, indicating that the homogeneous character increases with increasing iron content.

The retention of chemical composition was tested by the EDX analysis, which reveals a slight reduction in the iron content (1.86% for Fe(2)SZ and 9.58% for Fe(10)SZ). Recycling resulted in a gradual lowering of iron content and after five regenerations the iron content obtained was 1.58 and 5.32% for Fe(2)SZ and Fe(10)SZ respectively. This suggests that the catalyst is chemically stable at low iron loading perhaps due to the fine dispersion of the iron particles on the surface. The appearance of monoclinic phase in Fe(10)SZ during recycling may be a consequence of the reduction in the iron content. The XRD patterns of fresh samples reveal traces of monoclinic phase at iron loadings beyond 6%.

Influence of moisture

The catalyst after activation followed by exposure to moisture was used for the catalytic run. The negative influence of moisture on catalytic activity lends support to our assumption that Lewis sites are involved in the reaction. The conversion was reduced from 93.3 to 84.6% in presence of moisture.

Mechanism of the reaction

The percentage conversion obtained correlates with the Lewis acidity of the systems. The progressive increase in the catalytic activity with the increase in calcination temperature and the detrimental influence of moisture substantiates the involvement of Lewis acid sites in the reaction. The increase in Lewis acidity was rather sharp when the iron loading was varied. However, such a sharp rise could not be observed in the percentage conversions obtained. This may be an indication of the fact that the iron content or the Lewis acidity is not the only factor favouring the reaction. Also the sharp shooting of the catalytic activity for a temperature change of 10°C (in the interval 60°C to 70°C) cannot be discarded as a mere temperature effect. At 50°C and 60°C, the conversions obtained were very low. At 70°C, a drastic rise in the percentage conversion was obtained. Such a leap was not discernible in the case of simple sulphated system. This suggests the involvement of a different reaction mechanism. A plot of the catalytic activity as a function of reaction time reveals an induction period, which was quite perceptible in the case of Fe systems. The induction period was considerably shortened in samples with high iron loading.

Considering all the aspects, we propose the existence of a redox or a free radical mechanism in the case of Fe promoted samples along with the involvement of Lewis acid sites. Radicals are powerful reductants, which can readily be oxidised to cations in presence of reducible metal cations. Thus the high activity associated with these reducible cations involves the initiation of the reaction by the
homolytic cleavage of the C-Cl bond followed by the oxidation of the radical to the corresponding ions (Scheme 1). The possibility of a redox mechanism has been previously reported to explain the high activity obtained in catalysts containing reducible cations like Sn^{II}, Fe^{III} and Cu^{II}. At high iron loadings, the free radical mechanism may be considered to predominate as evident from the leveling off of the activities and the shortening of the induction period. The leaching out of iron may also be a consequence of the redox mechanism. It can be assumed that the energy of rupture prevents the free radical mechanism from operating at temperatures below 70°C. The activity at these temperatures may be due to the contribution of the Lewis acid sites.

Acknowledgement
The authors wish to express their sincere gratitude to CSIR, India for the fellowship awarded to SH.

References