Effective and Selective Heterogeneous Catalysts from Rice Husk Ash for the Benzylation of Some Aromatics

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Abstract

RHA-Ga, RHA-In and RHA-Fe heterogeneous catalysts were synthesized from rice husk ash (RHA) at room temperature using a sol-gel technique. All the catalysts were found to be amorphous, porous and have good textural properties as was depicted by physico-chemical characterization methods. The prepared catalysts were introduced for the benzylation of benzene (Bz) and some substituted benzenes with benzyl chloride (BC). The activity of the catalysts were found to be dependant primarily on the redox potential of the supported metal and decreases in the following order: RHA-Fe > RHA-In > RHA-Ga > RHA-Al. Interestingly these catalysts exhibited a reverse trend to that of the conventional Friedel-Crafts benzylation in the activity towards substituted benzenes. The catalysts are reusable and stable against leaching.

1. Introduction

Rice husk (RH), a waste product of the rice industry is rich in silica. It is well known that the RH contains 20% of ash and the silica content of this ash is 90 – 97% [1]. The large amount of silica freely obtained from rice husk ash (RHA) provides an abundant and cheap alternative source of silica which is useful for many applications particulary as a support for heterogeneous catalysis [2, 3].

Friedel-Crafts type alkylation of aromatic compounds using homogeneous Brønsted and Lewis acid catalysts are very well known in organic synthesis as an important means for attaching alkyl chains to aromatic rings [4]. The benzylation reactions of benzene and substituted benzenes are important for the production of diphenylmethanes (DPMs) and substituted DPMs which are used as intermediates in many industrial applications. This includes as plasticiser for vinyl resins, pharmaceutical, petrochemical, cosmetics, dyes and fine chemical as well as precursors in the production of dielectrics [5-10]. Due to the environmental problems accompanying this process, considerable efforts have been directed towards the heterogenization of these catalysts for the alkylation of benzene and substituted benzenes. The commonly used supports include mesoporous molecular sieves [11], zeolites e.g. ZSM-5 [12], clays [13], alumina [14] and poly acid salts [15].

In this work we attempt to study the benzylation of benzene (Bz) and some substituted benzenes with benzylchloride (BC) using heterogeneous catalysts prepared from RHA silica. The heterogeneous catalysts were synthesized by incorporating Al$^{3+}$, Ga$^{3+}$, In$^{3+}$ and Fe$^{3+}$ ions into silica from RHA. The results show that these catalysts are quite comparable to heterogeneous catalysts of different support materials reported for these reactions.
2. Experimental

2.1 Catalyst preparation

The treatment of RH and the preparation of the catalysts were done following the pathway previously reported by our group [2]. In a typical run, the treated RHA was dissolved in 1.0 M NaOH and filtered. The filtrate was titrated with 3.0 M HNO$_3$ solution (or containing the required percentages of Al$^{3+}$, Ga$^{3+}$, In$^{3+}$ or Fe$^{3+}$ ions) at a slow rate with constant stirring to pH 5. The gel formed was aged for 24 h. The precipitate was filtered, washed thoroughly with distilled water and dried at 100 $^\circ$C for 18 h. The silica or metal modified silica xerogel was ground to powder and labeled as RHA-SiO$_2$, RHA-5%Al, RHA-5%Ga, RHA-5%In, RHA-10%In, RHA-15%In and RHA-5%Fe.

2.2 Catalyst characterization

The prepared samples were characterized by FT-IR spectroscopy, N$_2$ sorption analysis, powder X-ray diffractometry, Scanning Electron Microscopy, Energy Dispersive Spectrometry (EDX) using the same instruments and methods stated in our previous publication [2]. The gas chromatograms of the benzylation products were collected from Clarus 500 GC instrument (Perkin Elmer) with a VB-1 non polar capillary column (30 m length and 0.32 mm inner diameter). The chromatogram was equipped with FID detector. The products were further confirmed with standards and GC-MS.

2.3 Catalytic reaction

Liquid phase Friedel – Crafts benzylation of benzene and substituted benzenes were carried out in a magnetically stirred round-bottomed flask equipped with a reflux condenser using an oil bath and thermometer. The reactions were set under continuous flow of argon. In a typical reaction, Bz or substituted benzenes and the internal standard were added to 0.1 g of the catalyst (which had been activated overnight at 100 $^\circ$C and flushed with Argon). The reaction mixture was maintained for 30 minutes at the predetermined temperature (75, 80 or 85 $^\circ$C). This was followed by the addition of BC to obtain the required CB/BC molar ratio keeping the total volume of the reaction mixture at 25.0 mL. Samples for analysis (~ 0.50 mL) were withdrawn at regular intervals from the reaction mixture and analyzed by gas chromatography.

3. Results & Discussion

3.1 Characterization

Nitrogen adsorption analysis showed that the textural properties of RHA-SiO$_2$ was retained after the surface modification of metal ions, since RHA-SiO$_2$ and RHA-Ga gave similar isotherms (type IV according to BET classification) and hysteresis loops type H1 (RHA-SiO$_2$, RHA-5%Al, RHA-5%Ga, RHA-5%In and RHA-5%Fe) or type H3 (RHA-10%In and 15%In) according to IUPAC classification. This analysis also showed that these heterogeneous catalysts had high BET surface area (272 – 384 m$^2$ g$^{-1}$), pore size (15.2 - 10.4 nm) and pore volume (1.08 - 0.82 cc g$^{-1}$) as shown in Table 1.

The low angle XRD (Fig. 1), TEM and SEM (not shown) revealed that the amorphous and porous structure of RHA-SiO$_2$ was retained after the incorporation of Al$^{3+}$, Ga$^{3+}$, In$^{3+}$ or Fe$^{3+}$ ions. Whereas FT-IR and EDX analysis (not shown) confirm these metal ions were attached to the silica surface and were homogenously distributed in the silica matrix if the loading of metal ions is 5%. However, further increase in the percentage of metal loading resulted in
non-homogeneous distribution of metal ions on the catalyst surface or network. In addition increasing the metal content resulted in the progressive decrease in the surface area as shown in Table 1 for RHA-In.

Table 1: The BET analysis parameters and metallic ion content (by ICP-MS) for RHA-SiO$_2$, RHA-Al, RHA-Ga and RHA-Fe.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area, S ($\text{m}^2 \text{g}^{-1}$)</th>
<th>BJH average pore Volume ($\text{cc g}^{-1}$)</th>
<th>BET average pore diameter (nm)</th>
<th>Average metal ions (w/w) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA-SiO$_2$</td>
<td>347</td>
<td>0.872</td>
<td>10.4</td>
<td>-</td>
</tr>
<tr>
<td>RHA-Al</td>
<td>384</td>
<td>0.452</td>
<td>5.2</td>
<td>5.1</td>
</tr>
<tr>
<td>RHA-Ga</td>
<td>332</td>
<td>0.824</td>
<td>10.4</td>
<td>2.5</td>
</tr>
<tr>
<td>RHA-Fe</td>
<td>284</td>
<td>1.08</td>
<td>15.2</td>
<td>3.7</td>
</tr>
<tr>
<td>RHA-5%In</td>
<td>272</td>
<td>0.873</td>
<td>12.9</td>
<td>2.8</td>
</tr>
<tr>
<td>RHA-10%In</td>
<td>209</td>
<td>0.986</td>
<td>15.4</td>
<td>8.4</td>
</tr>
<tr>
<td>RHA-15%In</td>
<td>114</td>
<td>0.415</td>
<td>13.4</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Fig. 1: The X-ray diffraction spectrum of (a) RHA-Al, (b) RHA-Ga (c) RHA-In and (d) RHA-Fe.

3.2. Catalytic reactions

The catalyst shows high catalytic activity and selectivity for the benzylation reactions of benzene and substituted benzenes. The activity of the catalyst was found increased with increasing the reaction temperature (Fig. 2). However, the selectivity to DPM products follows the opposite trend. Fig. 3 shows that increasing the loading of In$^{3+}$ ions from 5% to 10% was found to increase the percentage conversion of BC significantly. But further
increases of the metal concentration to 15% only resulted in a slight increase in the percentage conversion. Therefore, metal loading beyond 10 % was found to be not advantageous.

![Graph of reaction profile](image)

**Fig. 2.** The reaction profile of Bz and BC over RHA-In at different temperatures using Bz/BC molar ratio of 15:1.

![Graph of reaction profile](image)

**Fig. 3.** The reaction profile of Bz and BC at 80 °C over RHA-In catalyst with different loading of indium ions using Bz/BC molar ratio of 15: 1.

The catalytic activity of RHA-Al, RHA-Ga, RHA-In and RHA-Fe was tested in the benzylation of benzene employing benzyl chloride as the alkylating agent. It is very obvious from Table 2 and 3 that RHA-Fe exhibited the highest catalytic activity whereas RHA-Ga and
RHA-In showed the highest selectivity to DPM. The activity of these catalysts was found consistent with the redox potentials of supported metals rather than their Lewis acidity and it was found follows the order: RHA-Fe > RHA-In > RHA-Ga > RHA-Al. The negative behavior of RHA-Al could be attributed to many reasons including the extremely high sensitivity of supported Al\(^{3+}\) ions to moisture and the low redox potential of these metallic species.

Table 2: The product distribution with different catalysts for the reaction at 80 °C and Bz/BC ratio of 15:1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>50 % BC conversion</th>
<th>90 % BC conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (min)</td>
<td>Selectivity (%)</td>
</tr>
<tr>
<td>RHA-Al</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RHA- Ga</td>
<td>46</td>
<td>91.0</td>
</tr>
<tr>
<td>RHA- In</td>
<td>28</td>
<td>90.5</td>
</tr>
<tr>
<td>RHA- Fe</td>
<td>6.3</td>
<td>87.5</td>
</tr>
</tbody>
</table>

Table 3: The kinetic parameters for benzylation of benzene over different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>k at 80 °C (min(^{-1}))</th>
<th>E(_a) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA- Ga</td>
<td>24.5 ×10(^{-3})</td>
<td>26.4</td>
</tr>
<tr>
<td>RHA- In [2]</td>
<td>63.0 ×10(^{-3})</td>
<td>22.9</td>
</tr>
<tr>
<td>RHA- Fe</td>
<td>210 ×10(^{-3})</td>
<td>17.6</td>
</tr>
</tbody>
</table>

The benzylation of substituted benzenes was tested over RHA-In. the results illustrated in Fig. 3 indicate the trend in the activity towards these aromatics is completely opposite to that observed for the classical acid catalyzed Friedel-Crafts (FC) type benzylation reactions. An explanation for this had been given in [2]. The absence of any products when RHA-In was used in the reaction with anisole in the prescribed conditions was suggested to be due to the strong adsorption of anisole on the catalyst surface.

It is interesting to note that the reaction process stopped when the catalyst was omitted from reaction mixture during the course of the reaction (leaching test) as depicted in Table 4. Accordingly, it is safe to conclude that a purely heterogeneous rather than homogeneous catalytic reaction was taking place when RHA supported metals were used as catalysts. Furthermore these catalysts can be reused for the benzylation reaction several times without any significant change in their activity and selectivity as shown in Fig. 4.
Fig. 3: The effect of electron donating substituents for the benzylation over RHA-In at 80 °C, molar ratio of 15:1 and 50 min using different substituted benzenes. (Et benz = ethylbenzene)

Table 4: Leaching effect for RHA-In at 80 °C and Bz/BC reactant ratio of 15:1.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>BC conversion %</th>
<th>DPM %</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>57</td>
<td>89.4</td>
</tr>
<tr>
<td>55*</td>
<td>60.5</td>
<td>88.9</td>
</tr>
</tbody>
</table>

* Reaction after RHA-In catalyst has been removed.

Fig. 4 Re-usability of RHA–In catalyst (0.1 g) at 80 °C and Bz/BC molar ratio of 15:1.
3. Conclusion

The catalytic activity of RHA-Al, RHA-Ga, RHA-In, and RHA-Fe were tested in the benzylation benzene employing BC as the alkylating agent. RHA-Fe catalyst showed the highest catalytic activity whereas RHA-In and RHA-Ga catalysts gave higher selectivity to DPM. The catalytic activity followed the order: RHA-Fe > RHA-In > RHA-Ga > RHA-Al. RHA-In also showed good activity for the benzylation of some substituted benzenes, however, the trend was found oppose the traditional FC reaction. Increasing the In\(^{3+}\) ion loading from 5 to 10 % was found to accelerate the catalytic activity drastically whereas further increase in In\(^{3+}\) ion loading showed only marginal change in activity or in the selectivity. The catalysts could be reused for the benzylation reaction several times without significant change in their activity and selectivity. These catalysts are comparable to those of other supports so far reported in the available literature.

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References: