Alkylation of benzene with isopropanol on mixed oxides

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A comparative study of the reaction involving the vapour phase isopropylation of benzene with isopropanol over mixed oxide catalysts with spinel structure is taken up to evaluate the performance of these potential catalysts for the industrially important cumene synthesis. Their activity is compared in the temperature range 473-553 K and with two different mole ratios of benzene to isopropanol. The major product is cumene but it has been observed that at high temperature dialkylation occurs. A laboratory scale fixed bed flow reactor has been used at atmospheric pressure for the experiments.

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Cumene is an intermediate for the industrial production of phenol and acetone. The two available industrial processes have problems of corrosion, waste treatment and exhaust catalyst disposal. This accounts for the efforts devoted to the research of more efficient, safe and environment-friendly catalysts. Several catalytic processes using various types of zeolites\textsuperscript{1-3}, alkali exchanged zeolite\textsuperscript{4}, SAPO-S\textsuperscript{5} are reported to be able to catalyse this reaction. Two commercial cumulative processes have been developed by Mobile and CDTECH, respectively. The first one operates in a fixed bed reactor system using ZSM-5 zeolite as catalyst\textsuperscript{6,7} and a second in a catalytic distillation column reactor using Y-type zeolite\textsuperscript{8}. However, the rapid ageing of zeolitic catalysts is still an essential problem to resolve. Lately, the development of a new cumene process based on a highly dealuminated mordenite has been reported\textsuperscript{9}. Though the reaction can be operated at moderate temperatures in liquid phase conditions, the separation of products is often difficult. In this work, the alkylation of benzene with isopropanol in vapour phase conditions has been investigated on a series of mixed metal oxides crystallizing with spinel lattice, of third transition series such as CuFe\textsubscript{2}O\textsubscript{4}, ZnFe\textsubscript{2}O\textsubscript{4}, CoFe\textsubscript{2}O\textsubscript{4} and NiFe\textsubscript{2}O\textsubscript{4}. The choice of catalyst as a spinel system is due to two reasons, first, spinel lattice imparts extra stability to the catalyst under various reaction conditions. Secondly, mixed metal oxides do not lose their catalytic activity due to aging and formation of carbon over the surface so these systems have sustained activities for longer duration\textsuperscript{10}.

Experimental

Nitrates of zinc, copper, cobalt, nickel and iron of analytical reagent grade were used for catalyst preparation. (30\%) H\textsubscript{2}O\textsubscript{2}, SiO\textsubscript{2} of mesh size 60-200 were used; ZrO\textsubscript{2} was prepared from zirconyl oxychloride according to procedure mentioned elsewhere\textsuperscript{11}. Benzene and isopropanol of analytical grade were used without further purification. The catalyst was prepared using co-precipitation technique\textsuperscript{12,13}.

To prepare the catalyst an aqueous solution containing the desired ions in the required molar proportions was prepared by dissolving the salts in the stoichiometric proportion in distilled water. It was precipitated by sodium hydroxide and the pH of the solution was maintained between 9 to 9.5. The precipitate was digested at 80°C in water bath for 3 h and then oxidized by dropwise addition of required amount of 30\% H\textsubscript{2}O\textsubscript{2} with constant stirring. After completion of reaction the resultant precipitate was filtered and washed with distilled water to remove excess of alkali and nitrate ions. The precipitate was dried at 110°C for 3 h then calcined at 900°C for 9 h.

Spinel synthetized by this method have high surface area\textsuperscript{14}. The 10\% catalyst supported on SiO\textsubscript{2} and ZrO\textsubscript{2} were prepared by impregnating the aqueous solution of nitrates of required ion in a stoichiometric amount on the support; they were at 120°C and calcined at 900°C for 9 h.

All the catalysts were characterized by X-ray powder diffraction. The diffraction patterns were recorded on Siemens D-500 Kristallosflex diffractometer with a microprocessor controller using CuK\textalpha radiation with nickel filter.

LS particle size analyzer (COULTER COUNTER) was used for particle size measurement.
Reaction procedure

Each catalyst was studied for its catalytic behaviour towards alkylation of benzene with isopropanol in the temperature range 473-553 K using fixed bed flow glass reactor (30x1.4 cm), catalyst (1.0 g) was placed on a porcelain septum fused at the centre of the reactor tube. The reactor was covered with a thermocouple to measure the temperature at the catalyst bed. Reactants were fed from the top of the reactor using a syringe pump (SAGE, USA) that can be operated at different flow rates. A stream of N₂ gas was passed from the top of the reactor. The products were condensed by circulating ice-cold water through condenser from circulating bath (Masterline model no. 2095).

The products were analyzed by G.C. (Chemito model no. 8610) fitted with methyl silicon column and checked by TLC using silica gel.

Results and discussion

X-ray diffraction patterns of all the compositions (Fig.1) showed the formation of single-phase spinel and matched well with standard JCPDS patterns.

Particle size analysis shows that SiO₂ supported catalyst has more surface area than ZrO₂ supported catalyst (Table 1).

The efficiency of different catalysts was evaluated at 473 K with 1.0 g of catalyst loading, 0.1 ml/min of feed rate and benzene to isopropanol in mole ratio 5. As summarized in Table 2 it can be seen that only Cu containing catalyst gives the alkylation product of benzene. CuFe₂O₄ shows better conversion and selectivity compared to CuO and Cu₀.₅Zn₀.₅Fe₂O₄.

To study the effect of mole ratio the alkylation reaction was studied at different mole ratios of benzene to isopropanol at 473 K with catalyst loading of 1.0 g and feed rate 0.1 ml/min. It was observed that with increase in mole ratio from 5 to 7 the conversion rate of isopropanol decreases with CuFe₂O₄ as shown in Table 3.

The efficiency of CuFe₂O₄ at different temperatures were studied with 1.0 g loading of catalyst, mole ratio of benzene to isopropanol is five and feed rate 0.1 ml/min. It was observed that with increase in temperature from 473 to 553 K, conversion of isopropanol increases but selectivity towards cumene was high at 513 K beyond which selectivity decreased due to dialkylation of benzene as shown in Table 4.

To see the effect of support in alkylation of benzene, CuFe₂O₄ was supported on SiO₂ and ZrO₂.
Table 3—Effect of mole ratio (Temp: 473 K; Amount of catalyst: 1 g; Feed rate: 0.1 ml/min)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>IPA % conversion at mole ratio 5</th>
<th>IPA % conversion at mole ratio 7</th>
<th>Cumene % selectivity at mole ratio 5</th>
<th>Cumene % selectivity at mole ratio 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe₂O₄</td>
<td>30.0</td>
<td>12.0</td>
<td>82.0</td>
<td>82.0</td>
</tr>
<tr>
<td>Cu₅Zn₅Fe₂O₁₄</td>
<td>17.0</td>
<td>25.0</td>
<td>81.0</td>
<td>81.0</td>
</tr>
</tbody>
</table>

Table 4—Effect of temperature (CuFe₂O₄: 1 g; Mole ratio: benzene:IPA 5; Feed rate: 0.1 ml/min)

<table>
<thead>
<tr>
<th>Temp. in K</th>
<th>IPA (% conversion)</th>
<th>Cumene (% selectivity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>30.0</td>
<td>82.0</td>
</tr>
<tr>
<td>493</td>
<td>50.3</td>
<td>83.0</td>
</tr>
<tr>
<td>513</td>
<td>60.8</td>
<td>83.1</td>
</tr>
<tr>
<td>533</td>
<td>74.7</td>
<td>82.1</td>
</tr>
<tr>
<td>533</td>
<td>8.0</td>
<td>82.0</td>
</tr>
</tbody>
</table>

Table 5—Effect of support (Temp: 473 K; Mole ratio: benzene:IPA 5; Feed rate: 0.1 ml/min)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>IPA (% conversion)</th>
<th>Cumene (% selectivity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe₂O₄</td>
<td>25.0</td>
<td>82.0</td>
</tr>
<tr>
<td>CuFe₂O₄/ZrO₂</td>
<td>48.0</td>
<td>86.0</td>
</tr>
<tr>
<td>CuFe₂O₄/SiO₂</td>
<td>55.0</td>
<td>89.0</td>
</tr>
</tbody>
</table>

Alkylation was carried at 513 K with 1 g of catalyst, mole ratio of benzene to isopropanol 5 and feed rate of 0.1 mL/min. The observations are noted in Table 5. It was seen that CuFe₂O₄/SiO₂ gave better conversion and selectivity than CuFe₂O₄/ZrO₂ due to increase in surface area.

To conclude, the alkylation of benzene with isopropanol was studied systematically using Cu₅Zn₅Fe₂O₁₄, Zn₁₀Ni₁₀Fe₂O₄, Zn₁₀Co₁₀Fe₂O₄, CuFe₂O₄, ZnFe₂O₄, CoFe₂O₄, NiFe₂O₄, CuO and Fe₂O₃. Only Cu containing oxides showed conversion of isopropanol. Amongst copper containing oxides CuFe₂O₄ showed better conversion rate and selectivity towards cumene at 513 K above this temperature selectivity towards dialkylation increases. CuFe₂O₄/SiO₂ was more efficient than CuFe₂O₄/ZrO₂ due to increased surface area.

References