Vapour phase isopropylation of biphenyl over modified molecular sieve catalysts

G Kamalakar, M Ramakrishna Prasad, S J Kulkarni* & K V Raghavan

Catalysis Group, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 27 October 1998; accepted 13 January 1999

The vapour phase isopropylation of biphenyl was carried over modified Y, SAPO and MCM-41 molecular sieves. The conversions of biphenyl were in the range of 31-77% and the selectivities of dialkylated biphenyl were 35-53%. The effect of various reaction parameters like reaction temperature, weight hourly space velocity, molar ratio were studied. The dialkylated products were more over MCM-41 catalyst and the ratio of monoalkylated/dialkylated in the products varied with the catalyst and time on stream.

A large number of alkylation reactions have been carried out over zeolites. Sugi and Toba reported liquid phase isopropylation of biphenyl over HM, HY zeolites. Kamalakar et al. carried out the alkylation of naphthalene or 1-naphthol with methanol, ethanol, isopropanol, butanol, over zeolites to develop eco-friendly processes. 4,4'-Diisopropylbiphenyl is used in the synthesis of thermoplastic materials, liquid crystal polymers and as membrane materials. In this paper the isopropylation of biphenyl with isopropanol over modified Y, SAPO-5 and MCM-41 molecular sieve catalysts has been reported.

Experimental Procedure

HY(Si/Al=2.5) zeolite was obtained from PQ corporation, U.S.A. MCM-41 and Silicoaluminophosphate-5(SAPO-5) catalysts were prepared according to the procedure reported in literature. The catalysts were highly crystalline and the XRD patterns were as per the literature. The surface areas of the catalysts are presented in the Table I. Due to the impregnation of various cations, the surface area was decreased.

The isopropylation of biphenyl was carried out over various catalysts and the results are presented in Table 2. The reactions were carried out at 250°C with 0.5 h⁻¹ weight hourly space velocity and biphenyl:isopropanol = 1:6 molar ratio. The maximum selectivities for total diisopropylbiphenyl were 53.1, 48.8, 52.7 and 53.3% at 64.0, 40.0, 62.0 and 77.2% conversions over FeHNaY, LaKY, CeKY and HMCM-41 molecular sieves respectively. The major product in total diisopropylbiphenyl was 4,4'-diisopropylbiphenyl. The ratio of mono- and diisopropylbiphenyl was more in case of Y-zeolite compared to MCM-41 due to shape selectivity. In other products triisopropylbiphenyl were present.

The effect of reaction temperature was studied and the results are given in Table 3. The catalyst used was FeHNaY zeolite. The maximum conversion to the dialkylated product was obtained in the temperature range of 250°C with 0.5 h⁻¹ weight hourly space velocity and biphenyl:isopropanol = 1:6 molar ratio. The maximum selectivities for total diisopropylbiphenyl were 53.1, 48.8, 52.7 and 53.3% at 64.0, 40.0, 62.0 and 77.2% conversions over FeHNaY, LaKY, CeKY and HMCM-41 molecular sieves respectively. The major product in total diisopropylbiphenyl was 4,4'-diisopropylbiphenyl. The ratio of mono- and diisopropylbiphenyl was more in case of Y-zeolite compared to MCM-41 due to shape selectivity. In other products triisopropylbiphenyl were present.

The effect of reaction temperature was studied and the results are given in Table 3. The catalyst used was FeHNaY zeolite. The maximum conversion to the dialkylated product was obtained in the temperature range of 250°C with 0.5 h⁻¹ weight hourly space velocity and biphenyl:isopropanol = 1:6 molar ratio. The maximum selectivities for total diisopropylbiphenyl were 53.1, 48.8, 52.7 and 53.3% at 64.0, 40.0, 62.0 and 77.2% conversions over FeHNaY, LaKY, CeKY and HMCM-41 molecular sieves respectively. The major product in total diisopropylbiphenyl was 4,4'-diisopropylbiphenyl. The ratio of mono- and diisopropylbiphenyl was more in case of Y-zeolite compared to MCM-41 due to shape selectivity. In other products triisopropylbiphenyl were present.

The effect of reaction temperature was studied and the results are given in Table 3. The catalyst used was FeHNaY zeolite. The maximum conversion to the dialkylated product was obtained in the temperature range of 250°C with 0.5 h⁻¹ weight hourly space velocity and biphenyl:isopropanol = 1:6 molar ratio. The maximum selectivities for total diisopropylbiphenyl were 53.1, 48.8, 52.7 and 53.3% at 64.0, 40.0, 62.0 and 77.2% conversions over FeHNaY, LaKY, CeKY and HMCM-41 molecular sieves respectively. The major product in total diisopropylbiphenyl was 4,4'-diisopropylbiphenyl. The ratio of mono- and diisopropylbiphenyl was more in case of Y-zeolite compared to MCM-41 due to shape selectivity. In other products triisopropylbiphenyl were present.

The effect of reaction temperature was studied and the results are given in Table 3. The catalyst used was FeHNaY zeolite. The maximum conversion to the dialkylated product was obtained in the temperature range of 250°C with 0.5 h⁻¹ weight hourly space velocity and biphenyl:isopropanol = 1:6 molar ratio. The maximum selectivities for total diisopropylbiphenyl were 53.1, 48.8, 52.7 and 53.3% at 64.0, 40.0, 62.0 and 77.2% conversions over FeHNaY, LaKY, CeKY and HMCM-41 molecular sieves respectively. The major product in total diisopropylbiphenyl was 4,4'-diisopropylbiphenyl. The ratio of mono- and diisopropylbiphenyl was more in case of Y-zeolite compared to MCM-41 due to shape selectivity. In other products triisopropylbiphenyl were present.

The effect of reaction temperature was studied and the results are given in Table 3. The catalyst used was FeHNaY zeolite. The maximum conversion to the dialkylated product was obtained in the temperature range of 250°C with 0.5 h⁻¹ weight hourly space velocity and biphenyl:isopropanol = 1:6 molar ratio. The maximum selectivities for total diisopropylbiphenyl were 53.1, 48.8, 52.7 and 53.3% at 64.0, 40.0, 62.0 and 77.2% conversions over FeHNaY, LaKY, CeKY and HMCM-41 molecular sieves respectively. The major product in total diisopropylbiphenyl was 4,4'-diisopropylbiphenyl. The ratio of mono- and diisopropylbiphenyl was more in case of Y-zeolite compared to MCM-41 due to shape selectivity. In other products triisopropylbiphenyl were present.

The effect of reaction temperature was studied and the results are given in Table 3. The catalyst used was FeHNaY zeolite. The maximum conversion to the dialkylated product was obtained in the temperature range of 250°C with 0.5 h⁻¹ weight hourly space velocity and biphenyl:isopropanol = 1:6 molar ratio. The maximum selectivities for total diisopropylbiphenyl were 53.1, 48.8, 52.7 and 53.3% at 64.0, 40.0, 62.0 and 77.2% conversions over FeHNaY, LaKY, CeKY and HMCM-41 molecular sieves respectively. The major product in total diisopropylbiphenyl was 4,4'-diisopropylbiphenyl. The ratio of mono- and diisopropylbiphenyl was more in case of Y-zeolite compared to MCM-41 due to shape selectivity. In other products triisopropylbiphenyl were present.

The effect of reaction temperature was studied and the results are given in Table 3. The catalyst used was FeHNaY zeolite. The maximum conversion to the dialkylated product was obtained in the temperature range of 250°C with 0.5 h⁻¹ weight hourly space velocity and biphenyl:isopropanol = 1:6 molar ratio. The maximum selectivities for total diisopropylbiphenyl were 53.1, 48.8, 52.7 and 53.3% at 64.0, 40.0, 62.0 and 77.2% conversions over FeHNaY, LaKY, CeKY and HMCM-41 molecular sieves respectively. The major product in total diisopropylbiphenyl was 4,4'-diisopropylbiphenyl. The ratio of mono- and diisopropylbiphenyl was more in case of Y-zeolite compared to MCM-41 due to shape selectivity. In other products triisopropylbiphenyl were present.
range of 200-250°C. The selectivities for ΣDIBP were 46.8, 49.7, 42.5 and 50.4 wt% at 64.1, 64.0, 50.8 and 25.0% conversions at 200, 250, 300 and 350°C respectively. Due to the coking at high (>300°C) temperatures the selectivity for ΣDIBP was increased and conversions and the other products were decreased. This is due to the decrease of active centres and the blocking of pores and cages.

The effect of weight hourly space velocity (WHSV) in the isopropylation of biphenyl was studied and the results were given in Table 4. The maximum selectivities for ΣDIBP were 46.2, 49.7, 53.0, 47.1 and 30.5 wt% at 63.0, 64.0, 55.4, 43.3 and 32.0% conversions at 0.25, 0.5, 0.75, 1.0 and 1.25 h⁻¹ WHSV respectively. At higher WHSV (~1.25 h⁻¹), ΣMIBP were more in the products. This is due to the coking and diffusion control. The trialkylated products were also decreased. The results of the variation of molar ratio in the feed are given in Table 5. The maximum selectivities for the ΣDIBP were 59.4, 53.0, 50.6, 50.2 and 61.3 wt% at 58.5, 64.0, 57.3, 53.2 and 60.8% conversions for 1:5, 1:6, 1:7, 1:8 and 1:9 molar ratio of biphenyl to isopropanol respectively. The reaction was carried out over (4g) FeΗNaY at 250°C with 0.5 h⁻¹ WHSV. The conversion and trialkylated products decreased with
Table 5—Isopropylation of biphenyl: Variation of molar ratio of feed

<table>
<thead>
<tr>
<th>Biphenyl</th>
<th>TOS h</th>
<th>Conversion of biphenyl wt%</th>
<th>Liquid product selectivity wt%</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 5</td>
<td>2</td>
<td>58.5</td>
<td>28.0, 59.4, 12.6</td>
<td></td>
</tr>
<tr>
<td>1 : 6</td>
<td>4</td>
<td>46.9</td>
<td>45.7, 52.0, 2.1</td>
<td></td>
</tr>
<tr>
<td>1 : 7</td>
<td>4</td>
<td>47.6</td>
<td>37.6, 42.6, 19.8</td>
<td></td>
</tr>
<tr>
<td>1 : 8</td>
<td>3</td>
<td>53.2</td>
<td>38.0, 50.2, 11.8</td>
<td></td>
</tr>
<tr>
<td>1 : 9</td>
<td>2</td>
<td>60.8</td>
<td>36.3, 61.3, 2.4</td>
<td></td>
</tr>
<tr>
<td>1 : 10</td>
<td>4</td>
<td>28.4</td>
<td>40.9, 57.1, 2.0</td>
<td></td>
</tr>
</tbody>
</table>

Catalyst: FeHNaY (5wt%Fe), biphenyl + isopropanol + Solvent (Benzene = 10 mL), ΣMIBP = Sum of monoisopropyl biphenyl products, ΣDIBP = Sum of diisopropyl biphenyl products, Other products = mainly trisopropylbiphenyl products, Catalyst weight: 4 g, Reaction temperature = 250°C, WHSV: 0.5 h⁻¹

the time. Due to coking the pore diameter decreased. With the increase in molar ratio with respect to isopropanol, there is an increase in the (dialkylated products) ΣDIBP/ΣMIBP ratio at the 4th hour on stream as given in Table 5.

The isopropylation of biphenyl was carried out for 14 h on stream over FeHNaY at 250°C with 0.5 h⁻¹ WHSV. The results are shown in Fig. 1. The yields of ΣDIBP were 32.0, 29.4, 14.7wt% at 60.7, 64.0 and 34.0% of conversions at 1, 2 and 14th hour on stream. Due to the coking, the conversion decreased from ~64% to 34.0 and the ratio of ΣMIBP/ΣDIBP increased from 1 to 1.37. The surface area, ammonia uptake and temperature programmed desorption of ammonia of LaHY, LaKY, etc. catalysts are given in reference discussing the isopropylation of naphthalene. The catalysts were crystalline before and after the reactions. The trend in total acidity derived from ammonia uptake at 125°C was LaHY > CeMgY > SAPO-5 > LaKY > CeMCM-41 > HMCM-41. To enhance the alklylation activity, the molecular sieves were modified by the cations like La³⁺, Ce³⁺ and Fe³⁺. The catalysts were further modified by the K⁺ or Mg²⁺ to optimize the acidity and reduce the coking. Considering the area under the ammonia TPD peak, the trend in the acidity was LaHY > SAPO-5 > HMCM-41 > LaKY > CeMCM-41. In the isopropylation of biphenyl the conversion of biphenyl is more in case of MCM-41 catalysts as given in Table 1. The correlation between acidity and activity is affected by the coking and extent of coking. In case of Y zeolite the types of coking are site poisoning and pore blocking. This may lead to the nonlinearity in the correlation.

Conclusion

In the isopropylation of biphenyl the following observations may be noted: (i) the dialkylated and trialkylated products were more over MCM-41 catalysts, (ii) the monoalkylated products were increased over coked Y, after 4th hour on stream, and (iii) the ratio of ΣMIBP/ΣDIBP varied with the catalyst and time on stream.

Acknowledgement

Authors are thankful to Department of Science & Technology, New Delhi for funding DST project No.
SP/S1/H07/97. GK is thankful to UGC, India for SRF.

References