Beckmann rearrangement of cyclohexanone oxime over modified molecular sieves

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The vapour phase Beckmann rearrangement of cyclohexanone oxime to \( \varepsilon \)-Caprolactum over silicoaluminophosphate (MSAPO-5, MSAPO-11) and MZSM-5 has been carried out. The yields of \( \varepsilon \)-Caprolactum were 72.0 and 81.5\% at 96.0 and 100\% conversion over ZnSAPO-11 and TiSAPO-11 molecular sieves, respectively.

\( \varepsilon \)-Caprolactum is the monomer for the synthesis of nylon-6 and is produced by the liquid phase Beckmann rearrangement of cyclohexanone oxime using concentrated sulphuric acid as a catalyst and solvent\(^1\). Although, this procedure is convenient from a chemical point of view, the large amount of ammonium sulphate formed during the subsequent neutralization of the oleum, the use of large amounts of fuming sulphuric acid and the corresponding problem of corrosion make this process environment non-friendly. The use of zeolite molecular sieves allow the production of desired products with less environmental pollution. The vapour phase Beckmann rearrangement of cyclohexanone oxime has been reported\(^2\) over solid acid catalysts including, alumina\(^3\), silica-alumina\(^4\), zeolite Y\(^5\), SAPO-11\(^6\) and MCM-41\(^7\). Beckmann rearrangement over SAPO-5 has not been investigated by others. In this paper, the vapour phase Beckmann rearrangement of cyclohexanone oxime to \( \varepsilon \)-Caprolactum over modified silicoaluminophosphate (SAPO-5, SAPO-11) molecular sieves has been investigated.

**Experimental Procedure**

Silicoaluminophosphate (SAPO) molecular sieves are synthesised in the laboratory as per literature\(^8\). MSAPO-11 was synthesised using Ti, Fe, Zn, Ni, Cu, Mn salts during synthesis. HZSM-5 catalyst was supplied by M/S Conteka, Sweden with SiO\(_2\)/Al\(_2\)O\(_3\) ratio 30. HZSM-5 was further modified with 5 wt\% of various cations like V, Cr, Cu, Pd and Mo by the impregnation method. The corresponding metal nitrates were used in this process. After impregnation the catalysts were washed with distilled water and dried at 100°C. The reactions were carried out using tubular, down flow, pyrex reactor with 20 mm internal diameter. The reactants were fed from top using sage syringe pump. The amount of catalyst was 4 g with 18-30 mesh size. The product was cooled by ice-cold water and collected at the bottom. The products were analysed by Gas-Chromatography using 10% SE-30 column and confirmed by mass spectra, GC-Mass and NMR. The mass balance of the liquid product was > 95\%.

**Results and Discussion**

The physicochemical characterization of the catalysts is reported elsewhere\(^9\). The Beckmann rearrangement (i.e. the transformation of ketoximes into amides) of cyclohexanone oxime was carried out using 10 wt\% cyclohexanone oxime in acetonitrile at 390°C and 0.5 h\(^{-1}\) weight hourly space velocity (W.H.S.V.) over modified SAPO-11 and SAPO-5 catalysts. The yields of caprolactum were 81.5, 72.0, 64.3 wt\% at 100, 96 and 100\% conversions over the Ti-SAPO-11, ZnSAPO-11 and Ni-SAPO-5 molecular sieves respectively, as given in Tables 1&2.

The reaction temperature was varied from 200 to 390°C in the rearrangement of oxime over Ti-SAPO-11 catalyst and the results are given in Table 3. The results of the catalyst performance with temperature show that with increase in temperature from 200°C to 390°C cyclohexanone oxime conversion increases and selectivity to caprolactum also increases. At 390°C, the conversion of oxime was 100\% with caprolactum selectivity 81.5\%. The by-products of this reaction were cyclohexanone, 5-cyanopent-1-ene. At lower
temperatures the formation of caprolactum decreases and the formation of by-product cyclohexanon e increases. As the temperature increases above 390°C, lower selectivity was noticed for caprolactum and this is due to the decomposition of caprolactum on the catalyst surface.

The reaction was also carried out using 10 wt% oxime in ethanol at 300°C reaction temperature and 0.5 h⁻¹ WHSV over modified ZSM-5 catalysts. The results obtained are given in Table 4. Among the various solvents tested over ZSM-5 catalyst, ethanol was the best solvent to accentrate the conversion of
oxime. Typically, the yields of caprolactum over HZSM-5 (30), VZSM-5, CrZSM-5, CuZSM-5, PdZSM-5 and MoZSM-5 were 41.4, 32.8, 57.5, 36.5, 49.5 and 40.0 wt% at 100% conversion of cyclohexanone oxime respectively. The other by-products formed in addition to cyclohexanone were 5-cyano pent-1-ene and ethyl caprolactum. The wt% yield of cyclohexanone, 5-cyano pent-1-ene and other products were given with respect to the best time on stream. Among the various catalysts studied over SAPO-11, SAPO-5 and ZSM-5, it was noticed that Ti-SAPO-11 and Cr-ZSM-5 are the superior ones. Caprolactum formation is catalysed by weak Bronsted acid sites.

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