Catalysis News

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Cyclohexanone to caprolactam in one step

Almost all of the caprolactam produced worldwide (about 3.8 million tons) is by the conc. H_2SO_4 catalyzed cyclization of cyclohexanone oxime. The most commonly used processes involve the preparation of cyclohexanone oxime from the ketone and hydroxylamine, and the Beckmann rearrangement of the oxime over conc. H_2SO_4. The manufacture of hydroxylamine involves many environmentally unfriendly procedures involving NOx, SO_2, H_2SO_4 and NH_3 (Rashig Process). Besides, the total production of byproduct $(NH_4)_2SO_4$ by the above route is about 45 Kg / Kg of caprolactam bringing down the overall atom efficiency of the process. Just the rearrangement of the oxime to caprolactam and subsequent neutralization of the acid produces about 1.4 Kg of $(NH_4)_2SO_4$ per Kg of caprolactam. Ammonium sulfate is not a desirable fertilizer (in the West) and its disposal poses difficulties. Hence, the development of greener and more atom efficient processes is very important. Recently, Sumitomo Chemical, Japan has demonstrated (in a 5000 tpa plant) a solid acid based process for the ammoximation of cyclohexanone to the oxime with NH_3 and H_2O_2 over a solid catalyst (TS-1) and the rearrangement of the oxime to caprolactam over another solid catalyst (MFI zeolite) [1]. The process does not produce any $(NH_4)_2SO_4$. There have been many attempts in the past to directly convert cyclohexanone into the oxime in the vapour phase over solid catalysts using NH_3 and O_2 (air). The most successful catalyst has been SiO_2 producing the oxime at about 40% selectivity at 200ºC [2]. Caprolactam was also reported to be formed in small amounts in the above reaction.

Very recently, Thomas and Raja have reported a single step conversion of cyclohexanaone into caprolactam in the liquid phase in the presence of O_2 (air) and NH_3 at 35 bar pressure and 80ºC (run duration, 8h) [3]. The catalyst reported by them is $ALPO_4$-5 containing two functions, an oxidation site to convert the cyclohexanone into the oxime and an acidic function to rearrange the oxime into caprolactam. The two functions have been introduced by incorporating two ions from the list, Si^{4+}, Mg^{2+}, Zn^{2+}, Mn^{3+}, Fe^{3+} and Co^{2+}. One of the ion acts as the acidic center and the other as the oxidation center. For example, over a MnMg $ALPO_4$-5 catalyst, they were able to obtain caprolactam directly from cyclohexanone at ~78% selectivity at ~68% conversion. Similarly, they have reported an oxime yield of ~87% at ~77% conversion over MnSi $ALPO_4$-5. This is a green and atom-efficient process for caprolactam production, the only by-product (in principle) being H_2O.

New methods for catalyst separation

One of the major disadvantages of homogeneous catalysts is their separation and reuse. Hence, much research has been focused on the heterogenization of homogeneous catalysts. Another approach to this problem is 'simuli-sensitive catalysts'. In one such example, the catalyst goes into solution in the reaction medium under reaction conditions (at a higher temperature) separating out from the medium at a lower temperature [4]. This is pictorially depicted in Scheme 1 (top picture). In this picture the catalyst is dissolved in the polar ionic liquid or a fluorous compound (say perfluorinated alkanes or ether) and the substrate is dissolved in the organic solvent. The substrate and the product have a low solubility in the polar phase while the catalyst is insoluble in the organic phase. At the conditions of the reaction (higher temperature), the two phases become miscible and the reaction takes place.

When the temperature is decreased at the end of the reaction, the two phases separate, the lower (heavier) polar phase containing the catalyst is separated and recycled [4].

Very recently, Hamamoto et al. have reported another system in which the catalyst separates from the reaction mixture on cooling (Scheme 1, bottom picture) [5]. In the case reported by them, the reaction medium is water and the catalyst is a thermophoric polymer supported phosphotungstic acid. The catalyst complex is insoluble in water at room temperature and forms an emulsion at 90ºC. This system has been used in the oxidation of alcohols with H_2O_2 as the oxidant. They have also shown the reusability of the catalyst at least three times. For example in the case of phenyl ethanol to acetophenone, the yield of the product was 92, 89 and 90% in the first three uses of the catalyst [5].
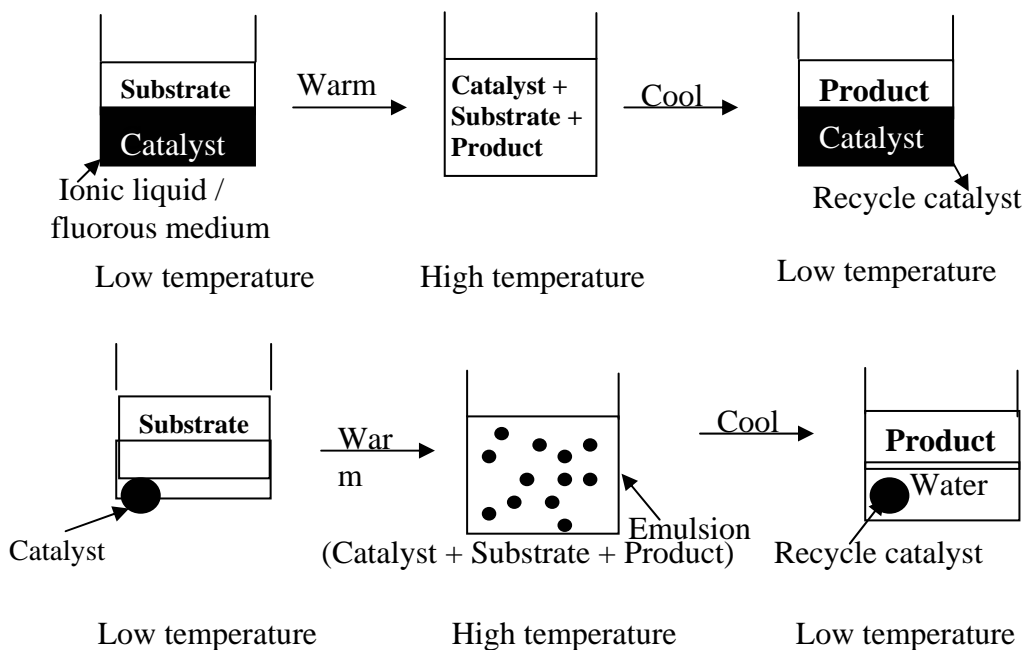
Scheme 1. Catalyst and product separation by thermophoric catalysts

Green solid acid alkylation of isobutene

Alkylates are produced by the reaction of isobutane with C_4 olefins (1- and 2- butene, especially) and are composed mainly of trimethyl pentanes. They possess an octane number of ~95. At present, alkylates are produced using anhydrous HF or conc. H_2SO_4 as catalysts. The total worldwide production of alkylates today is about 70 MMT per annum, approximately 40% of the capacity coming from HF processes and the rest from H_2SO_4 processes. Both the acid processes are not desirable due to dangers associated with corrosion and toxicity, environmental damage through waste products and process complexities. There has therefore been a continuous interest in a simpler, environmentally desirable solid acid catalyzed process. As of today, though many pilot plants are operating in the West, no commercial unit has been put up [6]. Very recently, a new processes called AlkyClean has been announced by ABB Lummus and Albermarle [8]. The alkylation is carried out at 50 – 90ºC over a zeolite based catalyst developed by Akzo Nobel. The process makes use of a swing reactor system with cycle lengths of 1 – 3 h between mild regeneration in H_2 at 250ºC. A pilot plant is running at Fortum's refinery at Porvoo in Finland. By far the greatest success on solid acid alkylation processes has been reported by UOP. They are presently in the process of designing a commercial plant of 30,000 tpa capacity at Baku, Azerbaijan. Their process called Alkylene involves alkylation in the presence of H_2, the regeneration being carried out in a separate vessel using again H_2 [7].

Utilization of glycerol

The increasing production of green diesel from vegetable oils is expected to lead to surplus availability of glycereol. One simple way of utilizing excess glycerol is steam reforming it into syn gas. However, glycereol is a highly functionalized compound and its transformation into a useful organic derivative is more preferred. Possible derivatives of glycerol are ethylene glycol and 1,3-propanediol (PDO), which are used in the production of polymers (polyesters). Mono ethylene glycol (EG) is prepared by the epoxidation of ethylene with air to ethylene oxide and its acid hydrolysis to ethylene glycol. 1,3-Propanediol is prepared by at least two methods [8]. In the first route, acrolein is hydrated to form 3-hydroxypropanal, which is next hydrogenated to PDO. In the second route, the intermediate 3-hydroxypropanal is obtained by the hydrocarbonylation of ethylene oxide. A third method that has not yet found commercial acceptance is the fermentation of glucose.

The transformation of glycerol into EG or PDO is an attractive route and could be an important green process of the future. The hydrogenolysis of glycerol into useful products has been reported by Kusunoki et al. recently [9]. They have used Ru-Amberlyst catalysts and have carried out the reactions at 4 or 10 bar H_2 pressure and temperatures in the range of 120 - 180ºC. Their results however are not very attractive, the major product in all the experiments being mostly 1,2-propanediol. The future holds much promise for catalysis research on value addition of glycerol.

Novel large surface area material

Férey et al. have described a highly porous material called MIL-101 (MIL, Matérial Institut Lavoisier) in a recent issue of Science [10].   The material is a chromium terephthalate-based solid. The measured pore volume was ~2 cm^3 g^{-1} and the **apparent** S_{BET} was 4,100 m^2g^{-1}.   The internal free diameters (cages) are reported to be 29 and 34 Å with windows of about 8.6 Å. The material has been found to be stable upto 275ºC in air (by thermogravimetry) and is not affected by many organic solvents. The authors have shown that it is possible to load catalytically active species like Keggin ions inside the void spaces.

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