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# Cation exchange resin-catalysed esterification of acetic acid with 2-(1-cyclohexenyl)cyclohexanone

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Self-aldol condensation of cyclohexanone yields a mixture of 2-(1-cyclohexenyl)cyclohexanone (I), 2-cyclohexylidenecyclohexanone (II) and subsequent condensation products. An acid-treated clay catalyst was employed to selectively obtain the $\beta,\gamma$-unsaturated ketone (I). (I) was separated from the reaction mixture by fractional vacuum distillation and subsequently esterified with acetic acid to synthesise the corresponding ester, 2-(2-cyclohexyl acetate)cyclohexanone, a precursor of [1,1-biphenyl]-2,2′-diol, which has applications in plasticizers, pesticides, as a diluent in epoxy resins, etc. The applicability of cation exchange resins and an acid-treated clay for the esterification of 2-(1-cyclohexenyl)cyclohexanone with acetic acid was explored.

**Keywords:** esterification, 2-(1-cyclohexenyl)cyclohexanone, acetic acid, cation exchange resin, acid-treated clay, 2-(2-cyclohexyl acetate)cyclohexanone

## 1. Introduction

The kinetics of aldol condensation of carbonyl compounds using homogeneous catalysts (acid/base-catalysed reactions) have been extensively investigated. However, these reactions are not well documented in the presence of solid acid or base catalysts. Heterogeneous catalysis offers, in many instances, higher yields and better selectivities under milder reaction conditions than an alternative homogeneous reaction medium. Furthermore, separation and effluent problems can be eliminated [1]. Acid-treated clays, in some cases, offer an inexpensive alternative to cation exchange resins. An exhaustive survey of the literature on various clay-catalysed reactions is given by Chitnis and Sharma [2]. Acid-treated clays have also been employed as heterogeneous catalysts in various alkylation reactions [3].

Aldol condensation of cyclohexanone with acid or base catalysts yields a mixture of compounds of which 2-(1-cyclohexenyl)cyclohexanone is of commercial importance. Shimizu et al. [4] reported that this aldol can be dehydrogenated on a Pt–KOH–$\gamma$-$Al_2O_3$ catalyst to give *o*-phenylphenol, which has potential industrial applications. *o*-phenylphenol is mainly used in dyes, drugs and in the manufacture of thermally stable and incombustible fibers. It is also useful as an anti-microbial agent, e.g., as a fungicide for the post-harvest treatment of citrus fruits. Moreover, when *o*-phenylphenol is admixed with other phenolics, it has been found to be effective in the formulation of synthetic detergent-disinfectant or germicidal agents [5].

Self-condensation of cyclohexanone yields a mixture of 2-(1-cyclohexenyl)cyclohexanone (I), 2-cyclohexylidenecyclohexanone (II) and subsequent condensation products. The use of ion exchange resins and clay catalysts for this reaction was studied by Shah et al. [6] to improve the selectivity of $\beta,\gamma$-unsaturated ketone (I). In the present work, the selectively obtained product, (I), was separated from the reaction mixture by fractional vacuum distillation and subsequently esterified with acetic acid to give the corresponding ester, 2-(2-cyclohexyl acetate)cyclohexanone, a precursor of [1,1-biphenyl]-2,2′-diol, which has applications in plasticizers, pesticides, as a diluent in epoxy resins, etc. The applicability of cation exchange resins and an acid-treated clay for the esterification of 2-(1-cyclohexenyl)cyclohexanone with acetic acid was explored.

No literature seems to be available on the esterification of 2-(1-cyclohexenyl)cyclohexanone with acetic acid using cation exchange resin and acid-treated clay as catalysts. However, substantial literature is available on the acid- or base-catalysed aldol condensation of cyclohexanone. Bell et al. [7] reported that the base-catalysed aldol condensation of cyclohexanone gives a mixture of 2-(1-cyclohexenyl)cyclohexanone, 2-cyclohexylidenecyclohexanone and higher condensation products. The synthesis of *o*-phenylphenol from cyclohexanone by condensation followed by dehydrogenation of 2-(1-cyclohexenyl)cyclohexanone over a Pt–KOH–$\gamma$-$Al_2O_3$ catalyst at 623 K was reported by Shimizu et al. [4]. Scheidt [8] has reported vapour-phase aldol condensation of cyclohexanone on alumina, lithium phosphate, lithium pyrophosphate and sodium orthophosphate. The liquid phase self-condensation of cyclohexanone in the presence of cation exchange resins, Dowex 50 [9] and Amberlite IR 120 [10] yields 2-(1-cyclohexenyl)cyclohexanone as the main product. However, the selectivity towards the desired product was not highlighted.

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Saha and Sharma [11] studied the esterification of formic acid, acrylic acid and methacrylic acid with a cyclic olefinic compound, namely cyclohexene, in batch and distillation column reactors using ion exchange resins as catalysts. Very recently, uncatalysed and catalysed (with cation exchange resins) esterification of formic acid and chloroacetic acid with another olefinic compound, viz. dicyclopentadiene (DCPD), i.e., 4,7-methano-3a,4,7,7a-tetrahydroindene, were studied by Saha and Sharma [12]. A similar reaction scheme was anticipated in the present work and therefore the study was directed towards investigation of the suitability of cation exchange resins and an acid-treated clay as catalysts. The effect of various parameters, e.g., speed of agitation, catalyst particle size, catalyst type, catalyst loading, temperature, mole ratio of the reactants, moisture on catalyst, catalyst reusability, etc., was studied to optimise reaction conditions.

## 2. Experimental

### 2.1. Materials

Cyclohexanone and acetic acid were obtained from M/s S.D. Fine Chem. Ltd., India. The reaction mass obtained from the self-aldol condensation of cyclohexanone (conversion $\sim$42%) at 393 K using Engelhard F-24 catalyst (20% w/w) was subjected to fractional vacuum distillation and the aldol, 2-(1-cyclohexenyl)cyclohexanone was obtained at very high purity (>99%). The aldol was characterised using $^1$H NMR. This self-aldol condensation product was treated as one of the raw materials for this reaction.

### 2.2. Catalysts

The acid-treated clay, Engelhard F-24 and the macroporous cation exchange resin, Amberlyst 15, were obtained from Engelhard Corporation, NJ, and Rohm and Hass, Philadelphia, PA, USA, respectively. Indion 130, which has properties very similar to those of Amberlyst 15, was obtained from Ion Exchange Ltd. (India), while Amberlite IR 120, a gelular cation exchange resin, was obtained from Fluka, Switzerland. Bayer K 2411 was supplied by Bayer, Germany. All the catalysts were dried under vacuum (2–3 mm Hg) at 373 K and stored under air-tight conditions before use. The physical properties of the catalysts employed for this reaction are listed in table 1.

Engelhard F-24, a montmorillonite clay, used in the present study is the aluminium-rich variety of dioctahedral smectite. The ideal structural formula of montmorillonite clay is $(Al_{3.15}Mg_{0.85})Si_8O_{20}(OH)_4X_{0.85}\cdot nH_2O$. The basic building blocks of clay minerals constitute the tetrahedral sheet of polymerised $SiO_4$ and the octahedral sheet of alumina. Like the $SiO_4$ tetrahedra, alumina octahedra can also polymerise in two dimensions by sharing four oxygen atoms which leaves two unshared oxygens giving a negative charge of two. The negative charge is counterbalanced in the natural state by hydrated cations, usually $Na^+$, $Mg^{2+}$, etc., which are situated in the interlamellar space. These interlamellar cations are generally exchangeable and their amount indicates the cation exchange capacity of the clay.

The acid strength of montmorillonite parallels the electronegativity of the exchanged cations. An aluminium species in three-fold coordination, perhaps occurring at an edge, or arising from a Si–O–Al rupturing dehydroxylation of the Brønsted site, corresponds to the Lewis site and functions as an electron pair acceptor. Water as a Lewis base can convert a Lewis site into a Brønsted site. Hence, the study of Lewis acidity is restricted to anhydrous systems.

The catalytic activity of acid-treated montmorillonite clay towards Brønsted and Lewis acid catalysed reactions is highly dependent on the degree of acid activation. Acid activation is generally accomplished by treating clays with concentrated mineral acids such as sulphuric, phosphoric or hydrochloric acids at an elevated temperature (ca. 368 K). The response of calcium montmorillonites towards acid activation is superior to sodium montmorillonites. Hence, they are generally preferred as raw materials in the manufacture of activated clay catalysts.

During the early stages of acid activation, the interlayer cations are likely to be exchanged for $H^+$ clusters and later by liberated $Al^{3+}$ and $Mg^{2+}$ ions from the octahedral sites. These cations relocate in the interlayer space and act as acid centres. Thus, acid activation promotes catalytic activity by increasing the number of Brønsted and potential Lewis acid sites. By simple washing with mineral acid, the surface acidity of natural montmorillonite as measured by Hammet acidity function ($H_0$) ranging from 1.5 to $-3.0$ is enhanced

Table 1
Physical properties of different catalysts.

| Physical property | Amberlyst 15 (macroreticular) | Indion 130 (macroreticular) | Bayer K 2411 (macroreticular) | Engelhard F-24 (acid-treated clay) | Amberlite IR 120 (gelular) |
|---|---|---|---|---|---|
| shape | beads | beads | beads | granular | beads |
| size (mm) | 0.5 | 0.55 | 0.5 | 0.66 | 0.5 |
| internal surface area ($m^2$/g) | 45.0 | a | 25.0 | 350.0 | a |
| weight capacity (meq/g) | 4.75 | 4.8 | a | 0.3 | 4.4 |
| crosslinking density (% DVB) | 20–25 | a | a | b | 8 |
| porosity (vol%) | 36.0 | a | 25.0 | 32.0 | no permanent porosity |
| temperature stability (K) | 393 | 393 | 403 | a | 393 |

[a] Data not available. [b] Not applicable.

to −5.6 to −8.0 [13]. As the intensity of the acid treatment is increased, the aluminium ion decreases progressively and the acidity initially increases, passes through a maximum and then decreases [14].

Organic ion exchange resins in acid form were used in this work. These were produced in the form of spheres of cross-linked polymers, i.e., polystyrene cross-linked with divinylbenzene (DVB) monomer. The copolymer beads were prepared by the pearl polymerisation technique. Sulphonic acid groups are introduced after polymerisation by treatment with concentrated sulphuric acid or chlorosulphonic acid. The main advantage of copolymer beads is that the degree of cross-linking and particle size are more readily adjusted in order to get tailor-made properties of the catalysts. The poly(styrene-DVB) resins can be broadly classified into two main groups based on the amount of DVB used in their preparation. They are gelular or gel-type resins and macroreticular or macroporous resins. Resins of both the categories have been studied in the present work.

Gelular resins are rigid, transparent, spherical beads and are not deformable, gelly-like materials as the name suggests. On a microscopic scale, the resin bead is a three-dimensional homogeneous structure with no discontinuities in the pore system. When the gelular resins are totally dry, the polymeric matrix collapses and the polystyrene chains are as close as atomic forces will allow. In these conditions, the resins are impervious to any molecule incapable of swelling the matrix, and therefore the catalytic activity of gelular resins is negligible unless the reaction is carried out in a swelling medium or the reactant is itself capable of swelling the matrix. As the reaction medium becomes more lipophilic, where particle swelling is less, the catalytic efficiency of a gelular resin diminishes drastically because the working gel phase is then only a small percentage of the total catalytic potential of the gel resin. Thus, the swelling ability of the reactants is a prerequisite for catalysis by gelular resins. The swelling of the gelular resins also depends on the degree of cross-linking and it increases as the cross-linking density is lowered.

Gelular resins are characterised by divinylbenzene contents below 12%. Highly cross-linked gelular resins are very poor catalysts because the matrix exhibits greater resistance to swelling. The divinylbenzene content of gelular Amberlite IR 120 resin used in this work was 8%.

The limitation of gelular resins, i.e., the necessity of using a matrix swelling medium, is overcome by macroporous resins. These resins have heterogeneous structures and consist of agglomerates of very small gelular microspheres. Each microsphere has a microporous matrix structure identical to that of common gelular resins, however, it is much smaller than typical gelular beads. These resins are prepared by polymerisation with high DVB content (5–60%) in the presence of diluents or porogens. During polymerisation, phase separation occurs and, after extraction of diluent and drying, permanent pores of various sizes are created.

The reactants can permeate easily into the pores of macroporous resins irrespective of whether the microspheres are swollen by solvent and/or reactants. There are many advantages of macroporous resins over gelular resins. The major one is that these resins are effective catalysts in both swelling and non-swelling solvents. Since these resins have a fixed pore structure even in the dry condition, the reactants can enter the body of the beads through the macropores contacting a large number of surface sulfonic acid sites. Thus, the reaction can take place even in the absence of microporous swelling. Another advantage of microporous resins over gelular resins is that they show excellent resistance to various types of attrition. Conventional gelular ion exchange resins shatter when some organic solvents replace water.

The ion exchange capacities (dry weight basis) of Indion 130, Amberlyst 15, Amberlite IR 120 and Engelhard F-24 are 4.8, 4.75, 4.4 and 0.3 meq/g, respectively. The acidity of Indion 130 is the highest amongst the materials studied. The particle size of Engelhard F-24 and Indion 130 range from 0.18 to 0.60 mm and the size range for Amberlyst 15, Amberlite IR 120 and Bayer K 2411 varied between 0.3 and 0.6 mm.

### *2.3. Experimental apparatus and procedure*

Batch experiments were carried out in a $10^{-4}$ $m^3$ capacity autoclave (Parr Instruments, USA) with an internal diameter of 0.05 m equipped with an in-built proportional-integral-derivative (PID) temperature controller. A four-bladed pitched turbine impeller was employed for agitation. The temperature was maintained at ±1 K of the desired value. The working volume of the reactor was typically around $6.5 \times 10^{-5}$ $m^3$. In a typical experiment, 50 g of total reactant molecules (in the required mole ratio) and 2.5 g of catalyst were charged to the reactor. However, the amount of acetic acid and 2-(1-cyclohexenyl)cyclohexanone was varied for experiments conducted at different mole ratios (e.g., 1 : 1 to 1 : 4). The temperature was raised to the desired value taking care to agitate only the liquid and not suspending the catalyst. The agitation was increased sufficiently to suspend the catalyst particles completely when the desired temperature was reached. This was noted as the starting time of the reaction. Samples were withdrawn periodically and analysed by gas chromatography.

### *2.4. Analysis*

Analysis of the reaction mixture was performed on a gas chromatograph (Chemito 8510, Toshniwal Brothers Ltd., India) equipped with a flame ionisation detector. A 2 m long column packed with 10% OV-17 on chromosorb-WHP was used for the analysis with nitrogen as the carrier gas at a flow rate of $5 \times 10^{-5}$ $m^3$/min. The injector and detector temperatures were kept at 673 K and the oven temperature was kept isothermal at 623 K.

## 3. Mechanism of reaction

In acid-catalysed aldol condensation of cyclohexanone, ion exchange resins or acid-treated clay catalyst act as a proton donor. It is assumed that aldol is first protonated to form a protonated ketone, which after tautomerism forms an enol. This enol attacks another protonated aldol molecule to form an intermediate which on subsequent deprotonation and dehydration forms 2-(1-cyclohexenyl)cyclohexanone and 2-cyclohexylidenecyclohexanone. The mechanism of acid-catalysed aldol condensation of cyclohexanone is given in figure 1.

In the esterification of 2-(1-cyclohexenyl)cyclohexanone with acetic acid in the presence of cation exchange resin, the protonated intermediate is formed (see figure 2). This intermediate is attacked by the lone pair of electrons of the oxygen atom of the hydroxyl group of acetic acid to form esters. Both esters (secondary and tertiary) can be formed depending on reaction conditions. However, the formation of tertiary ester is feasible only at very low reaction temperature. The protonated intermediate may combine with another intermediate to form the dimer of 2-(1-cyclohexenyl)cyclohexanone at higher temperature.

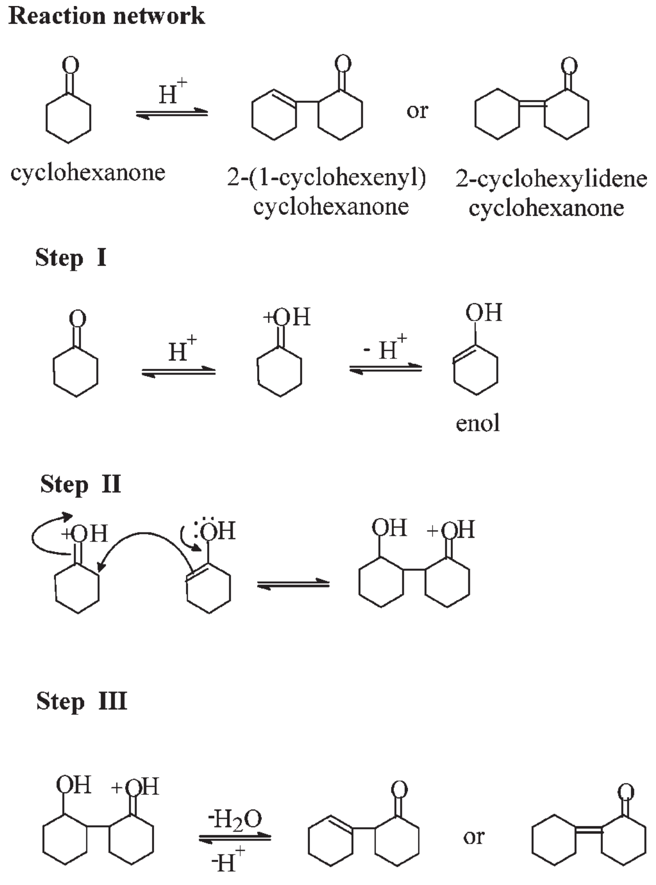

Figure 1. Mechanism of self-aldol condensation.

## 4. Results and discussion

Preliminary experiments were conducted varying the stirring speed (720–1200 rpm) to quantify the influence of external resistances to heat and mass transfer. These experiments showed that external diffusional limitations could be excluded at a stirring speed of 1000 rpm. Hence, all further experiments were conducted at a stirrer speed of 1100 rpm.

There does not seem to be any influence of the particle size on the reaction rate for Indion 130 catalyst with mean particle diameters 0.18–0.60 mm. It seems that there are no macropore diffusional limitations for the esterification reaction in the range of particle sizes studied.

The reactivity of any acid in the esterification reaction depends on its acidity. For the esterification of acetic acid with 2-(1-cyclohexenyl)cyclohexanone, the acidity of acetic acid ($pK_a = 4.77$) was not sufficient to catalyse the reaction in the absence of catalyst. Hence, different catalysts were employed for this reaction. The ion exchange capacities of Indion 130, Amberlyst 15, Amberlite IR 120 and Engelhard F-24 are 4.8, 4.75, 4.4 and 0.3 meq/g, respectively. The acidity of Indion 130 is the highest amongst the materials studied.

The effect of the catalyst was studied by carrying out the reaction of 2-(1-cyclohexenyl)cyclohexanone to acetic acid at 383 K (mole ratio 1 : 4) with Indion 130, Amberlyst 15, Bayer K 2411, Amberlite IR 120 and Engelhard F-24 catalysts (10% w/w). A similar level of conversion (~78%) of 2-(1-cyclohexenyl)cyclohexanone was obtained when macroporous Indion 130 and Amberlyst 15 resins were employed as catalysts. 66% selectivity towards the secondary ester was obtained at the end of 6 h of reaction. However, with Bayer K 2411, the level of conversion reduced to ~62% at the end of 6 h of reaction. The conversion of 2-(1-cyclohexenyl)cyclohexanone was negligible up to 383 K with Engelhard F-24 catalyst after 6 h. Macroporous resins (Indion 130 and Amberlyst 15) have higher capacities than Engelhard F-24, and hence, lower catalytic activity of the latter was observed. The conversion of 2-(1-cyclohexenyl)cyclohexanone was drastically reduced with Amberlite IR 120 catalyst probably due to its poor swelling characteristics in 2-(1-cyclohexenyl)cyclohexanone. Moreover, the lower exchange capacity (meq/g) of Amberlite IR 120 compared to macroporous resins may also reduce the conversion of 2-(1-cyclohexenyl)cyclohexanone. The conversion of 2-(1-cyclohexenyl)cyclohexanone exhibited by various catalysts is given in table 2. The best performance of Indion 130 can be attributed to its highest ion exchange capacity compared to other catalysts employed in this reaction.

The effect of catalyst loading was studied at 1 : 4 mole ratio of 2-(1-cyclohexenyl)cyclohexanone to acetic acid with Indion 130 catalyst at 393 K. The conversion of aldol increased from 72 to 78% with an increase in catalyst loading from 5 to 10% without any significant change in the selectivity towards the ester. The results are given in table 3.

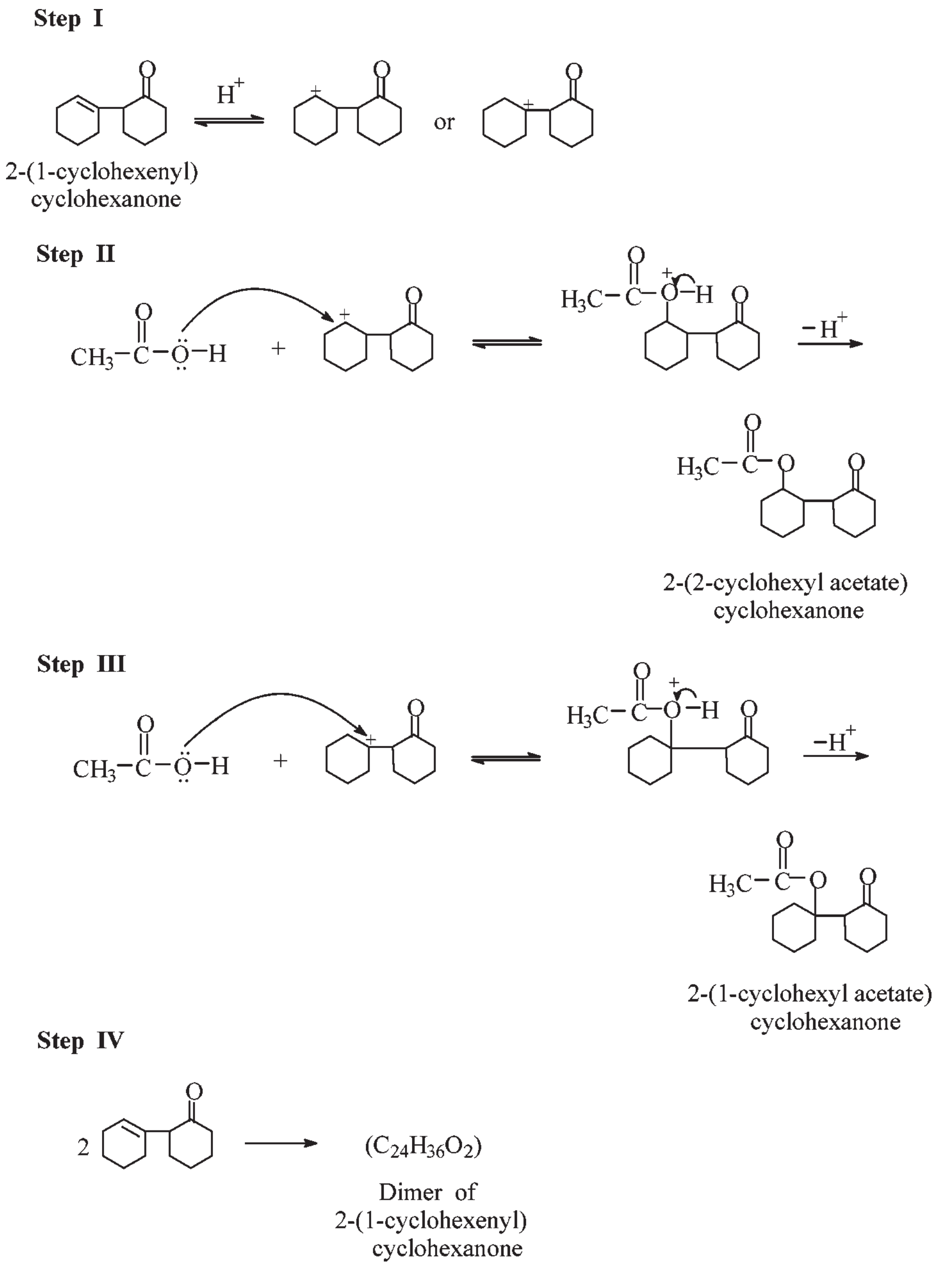

Figure 2. Mechanism of esterification reaction.

Table 2
Effect of catalyst on the esterification of 2-(1-cyclohexenyl) cyclohexanone with acetic acid.[a]

| Catalyst | % conversion (after 6 h) |
|---|---|
| Indion 130 | 78 |
| Amberlyst 15 | 76 |
| Bayer K 2411 | 62 |
| Amberlite IR 120 | 12 |
| Engelhard F-24 | negligible |

[a] Mole ratio (aldol : acetic acid): 1 : 4, temperature: 383 K, time: 6 h.

Table 3
Effect of catalyst loading on the esterification of 2-(1-cyclohexenyl)cyclohexanone with acetic acid.[a]

| Catalyst loading (%) | % conversion (after 6 h) |
|---|---|
| 5 | 72 |
| 10 | 78 |

[a] Catalyst: Indion 130, mole ratio (aldol : acetic acid): 1 : 4, temperature: 383 K, time: 6 h.

Temperature was varied from 333 to 383 K using Indion 130 as catalyst with 1 : 4 mole ratio of 2-(1-cyclohexenyl)cyclohexanone to acetic acid to assess its effect on the rate of esterification and selectivity towards the ester. At 333 and 343 K, no reaction took place under otherwise identical conditions. However, about 55% conversion of aldol was obtained at 373 K with 72% selectivity towards the ester. The rate of reaction as well as the conversion of 2-(1-cyclohexenyl)cyclohexanone increased to 78% at 383 K. However, the selectivity towards the

Table 4
Effect of temperature on the esterification of 2-(1-cyclohexenyl)cyclohexanone with acetic acid.[a]

| Temperature (K) | % conversion (after 6 h) | % selectivity (after 6 h) |
|---|---|---|
| 333 | nil | not applicable |
| 343 | nil | not applicable |
| 373 | 55 | 72 |
| 383 | 78 | 66 |

[a] Catalyst: Indion 130, catalyst loading: 10% (w/w), mole ratio (aldol : acetic acid): 1 : 4, time: 6 h.

Table 5
Effect of mole ratio on the esterification of 2-(1-cyclohexenyl)cyclohexanone with acetic acid.[a]

| Mole ratio (2-(1-cyclohexenyl)cyclohexanone : acetic acid) | % conversion (after 6 h) |
|---|---|
| 1 : 1 | 52 |
| 1 : 4 | 78 |

[a] Catalyst: Indion 130, catalyst loading: 10% (w/w), temperature: 383 K, time: 6 h.

ester reduced to 66% at 383 K compared to 373 K (see table 4). This was due to the formation of the dimer of 2-(1-cyclohexenyl)cyclohexanone at higher temperature.

The mole ratio of 2-(1-cyclohexenyl)cyclohexanone to acetic acid was varied from 1 : 1 to 1 : 4 with Indion 130 catalyst at 383 K. It can be seen in table 5 that the conversion of 2-(1-cyclohexenyl)cyclohexanone increased from 52 to 78% with a decrease in mole ratio from 1 : 1 to 1 : 4. This suggests that the esterification of acetic acid with 2-(1-cyclohexenyl)cyclohexanone is an equilibrium-limited reversible reaction.

The effect of moisture was studied for Indion 130 catalyst at 383 K and 10% w/w catalyst loading by carrying out experiments with undried (containing 1.0% w/w moisture) and dried resin. The presence of water had a detrimental effect on the rate of reaction. At low concentration of water in the resin phase, four sulphonic acid groups are attached to one water molecule [15]. Hence, the availability of the active sites on the catalyst surface decreases resulting in a sharp decrease in the rate of reaction. Moreover, water molecules permeate freely inside the pores of ion exchangers resulting in adsorption of water in the resin matrix [16]. The reaction conditions can be modified by substantially increasing the catalyst loading in order to achieve a similar level of conversion to compensate for low water concentration.

The catalysts were conveniently used up to 383 K without affecting their catalytic activities. For macroporous Indion 130 resin, the decrease in the selectivity towards the ester was observed at 383 K compared to 373 K due to the formation of a dimer of 2-(1-cyclohexenyl)cyclohexanone at higher temperature. However, the rate of reaction and the conversion of 2-(1-cyclohexenyl)cyclohexanone increased at 383 K.

Thermal degradation of the resins occurs due to desulphonation and it takes place significantly above 380 K. Fang [17] studied the stability of Amberlyst 15, a macroporous resin, in the temperature range 373–438 K and found that up to 413 K partial desulphonation occurs and at still higher temperatures, apart from desulphonation, shrinkage of the three-dimensional network takes place resulting in a hindrance for the access of reactant molecules to active sites.

Macroporous Indion 130 resin was reused up to five times (each time for a 6 h run) for this reaction. However, no significant change in the conversion of aldol and the selectivity towards the ester was observed. Hence, we can infer that these materials can be used repeatedly for this reaction without sacrificing catalytic activity. According to the manufacturer's specification, the lifetimes of ion exchange materials are normally about 10,000–16,000 operating hours when used at elevated temperatures.

## 5. Conclusions

Macroporous resins, Indion 130 and Amberlyst 15 can be used as catalysts for the esterification of 2-(1-cyclohexenyl)cyclohexanone with acetic acid at higher temperature (383 K). The reaction was unsuccessful with Engelhard F-24 up to 393 K. At 1 : 4 mole ratio of 2-(1-cyclohexenyl)cyclohexanone to acetic acid, the conversion of aldol was enhanced, however, the selectivity towards the secondary ester was reduced. The effect of moisture on the catalyst has a detrimental effect on the conversion of 2-(1-cyclohexenyl)cyclohexanone. Macroporous Indion 130 resin can be repeatedly used (five times) without losing catalytic activity towards this esterification reaction.

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