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Articles

The Effect of Dehydration in the Oxidation of Ethylbenzene to Acetophenone with Supported Catalysts

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Abstract:

The influence of the product water formed in the catalytic oxidation of ethylbenzene to acetophenone using air in a batch reactor was studied. The water adsorbed in the hydrophilic catalyst supports, that is, alumina or silica, has a significant negative effect on the oxidation processes. The application of a dehydration unit in the catalytic oxidation of ethylbenzene with air in a batch reactor was studied using sulphuric acid, molecular sieves, and silica gel as dehydrants. Processes were developed to use the dehydration unit to dehydrate the condensed product, from a Dean Stark trap, and the reaction mixture. Experimental results confirmed that an improvement in reaction performance was achieved using the dehydration unit to decrease the water concentration in the reaction mixture below its saturation solubility. The effect of a continuous increase in the temperature of the oxidation process, compared to isothermal operation, is shown to improve the oxidation performance.

1. Introduction

Many catalysts used in organic oxidation are based on metal ions immobilised on porous supports such as silica gel and alumina. The use of a heterogeneous catalyst, based on alumina-supported dichromate [EPAD (EPAD is the commercial name of the catalyst manufactured by Contract Catalysts, Knowsley Business Park, Merseyside)], for the oxidation of ethylbenzene to acetophenone with air has been recently reported.[1] A more recent communication reported a heterogeneous catalyst, based on silica gel-supported chromium (CHRISS), for the oxidation of the alkyl aromatics with air.[2] These studies showed that the oxidation was hindered by long induction periods and catalyst deactivation, which limited overall reaction rates. It has been reported that water acts as an inhibitor for catalytic organic oxidation,[3−6] due to the adsorption of water vapour on both the support and the metal ion sites, with the impact on the support being more significant than that on the catalyst sites.[4]

In this paper, the role of water in the oxidation of organic substrates with air using alumina- and silica-supported catalysts is discussed. The application of a dehydration unit for the catalytic oxidation of ethylbenzene to acetophenone with three dehydrants: sulphuric acid, molecular sieves, and silica gel, is described.

2. Microeffects of Water in Catalysts

The schematic representation of Cr ions bound on a chemically modified support surface is shown in Figure 1. The active Cr^{6+} (dichromate) or Cr^{3+} (chromium) cations used as catalysts are chemically immobilised on both external and internal surfaces of the supports, on which the catalytic reaction takes place. In the catalytic oxidation of ethylbenzene

$$\text{ethylbenzene} + \text{air} \xrightarrow{\text{EPAD or CHRISS}} \text{acetophenone} + \text{benzoic acid} + \text{water} \quad (1)$$

both ethylbenzene and oxygen must transfer from bulk liquid to the active Cr cation sites on both external and internal surfaces of solid supports, and acetophenone, benzoic acid, and water must transfer from the active Cr cation sites to bulk liquid.

On alumina the amount of chemisorbed water is proportional to the surface area, corresponding to binding of one H_2O to two O atoms in the surface. Additional water is adsorbed on the monolayer physically.[7] Study of dielectric behaviour of water adsorbed on γ-alumina suggested that in a multilayer system the first layer is strongly bound, while layers above the first freely orient in the applied field.[8] Bound water continues to be lost from γ-alumina even after heating to 1000 °C.[9] Aluminas used as catalyst supports are prepared by heating hydrated oxide to various temperatures so that

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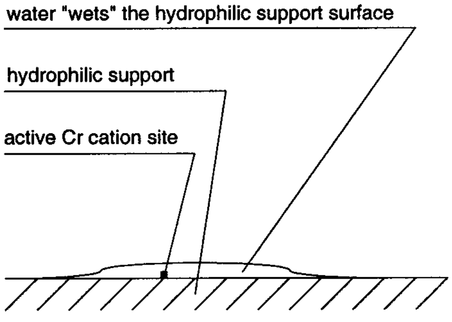

Figure 1. **Effects of water covering active Cr site.**

the surfaces may be partially or wholly dehydrated. The activity of the alumina depends critically on the pretreatment, subsequent exposure to moist air, and other factors.[10]

Silica gel, SiO_2, is a form of amorphous silica that is obtained by the hydrolysis of alkoxides such as $Si(OEt)_4$; it often contains ~4% water. Si NMR suggests the presence of $Si(OSi\equiv)_4$, $Si(OSi\equiv)_3(OH)$, and $Si(OSi\equiv)_2(OH)_2$ in silica gel.[11] Previous studies suggest that one water molecule is adsorbed for every two silanol groups on the gel surface. Loss of water from silica gel may begin at 50 °C, reaching a maximum rate of desorption at about 140 °C.[12]Due to the hydrophilicity of alumina and silica, water can wet the surface of the supports and be drawn into the mesopores. As the support is mesoporous (e.g., pore diameter 20 Å for EPAD, or 100 Å for CHRISS), there will be a considerable hydrostatic pressure due to the capillary rise.[13] This means that transfer of water from the mesopores is more difficult than that of ethylbenzene, which is the opposite the process requires.

For the three-phase catalytic oxidation of ethylbenzene (see eq 1) studied, product water has to be transported from the active sites of internal (and external) catalyst surface to the bulk liquid by diffusion. The driving force is the different water concentration between the active sites and the bulk liquid. In current industrial processes, to achieve required product specification, the water of reaction is usually removed by condensing the water and organic vapours in the reactor headspace.[14] With a Dean–Stark trap, or equipment operating on the same principle, condensed water is separated and removed while condensed organic (*that has a water concentration equal to its equilibrium solubility)* flows back to the reactor directly.

In a liquid aromatic reaction system with a Dean–Stark trap, the dissolved water concentration in the reaction mixture is quite low (e.g., at 18 °C and ambient pressure, the equilibrium solubility of water in ethylbenzene is ~300 ppm). However, additional removal of water, as proposed in this work, should benefit the reaction performance in terms of conversion, yield, and reaction rate.

Due to the hydrophilicity of alumina and silica supports, the catalysts can adsorb moisture from air during storage. In the first few hours of the ethylbenzene oxidation at ambient pressure and 130 °C, water is removed from the surface of the catalyst particles while the water in the core of the catalyst particles diffuses to the surface due to the water concentration gradient. This dehydration process removes the liquid water in the mesopores and the water released during the dehydration of alumina, enabling greater access of ethylbenzene to the Cr cation sites in the porous structure. The oxidation of ethylbenzene can hardly start until the catalyst is partially dehydrated, an “induction” period is usually observed.[1]

Assuming that the mass transfer rate of water, from catalyst sites to bulk liquid, is lower than the rate of production of water by reaction, water accumulation can lead to a thin “water film” covering, at least partially, the active Cr cation sites (Figure 1), which has significant negative consequences. As ethylbenzene is virtually insoluble and benzoic acid and acetophenone are only slightly soluble in water, a thin “water film” covering the active Cr^{5+} or Cr^{3+} sites will, at least, increase the mass transfer resistance for both reactants and products, or in the worst case, block the mass transfer completely and hence inhibit the oxidation process.

3. Experimental Section

3.1. Catalysts, Chemicals, and Sample Analysis. Catalysts were made according to the procedures previously described (EPAD[1] and CHRISS[2]). The dichromate/alumina catalyst EPAD has a dichromate loading of .~0.075 mmol g^{-1} (determined by atomic absorption spectroscopy), an average pore size of 20 Å, a particle size of 2–30 μm, and a surface area of 86.9 $m^2\ g^{-1}$. The chromium/silica catalyst CHRISS has a chromium loading of .~0.10 mmol g^{-1} (determined by atomic absorption spectroscopy), an average pore size of 100 Å and a particle size of 30–140 μm.

The chemicals used were GPR grade and obtained from Aldrich, England. Chemical analysis was by gas chromatography using a Unicam 610 system, with a capillary column and a FID detector.

3.2. Reactors. Two reactors were used in this study, a small glass reactor fabricated in-house and a computer-controlled autoclave.

The small reactor reaction system consisted of a 500 cm^3 vessel fitted with baffles, a stirrer, an air sparger, a reflux condenser, a decanter,and a heater (Figure 2). A thermocouple in the reactor was linked to a hot plate to control the temperature. A chiller was used to supply cooling water to the condenser at 0–1 °C to minimise loss of aromatic compounds from the reactor. Air was supplied to the reactor from a cylinder (industrial grade, obtained from BOC).

Initial studies of the oxidation of ethylbenzene considered the following ranges of parameters. The catalyst amount was changed from 0.125 to 5.0 g, air flow rate was changed from 200 $cm^3\ min^{-1}$ to 600 $cm^3\ min^{-1}$, temperature was changed from 115 °C to 130 °C, and agitator speed was changed from 500 to 2000 rpm, using 300 cm^3 of ethylbenzene and operating at atmospheric pressure. The preliminary “optimised” experimental conditions were

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(12) Darlow, B. B.; Ross, R. A. *Nature* **1963**, *198*, 988.

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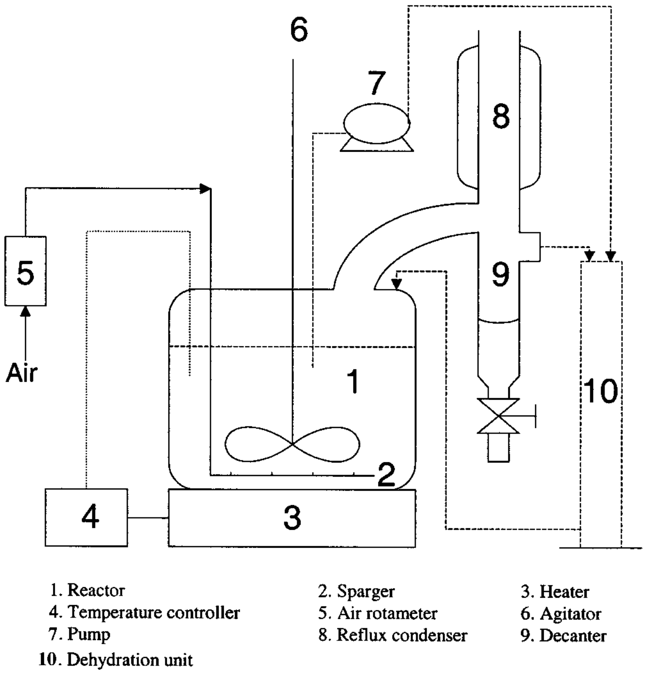

Figure 2. **Dehydration processes.**

amount of catalyst in reactor = 1.0 g
air flow rate = 400 cm^3 min^{-1}
temperature = 130 °C
agitator speed = 1500 rpm

All of the oxidations performed with the small glass reactor were carried out with the above experimental conditions unless otherwise indicated. Each test was carried out with fresh ethylbenzene, and the reactor was cleaned prior to each test.

The computer-monitored autoclave reactor consisted of a 1000 cm^3 glass autoclave (AE P/N 5010-2019 Glass Reactor, Autoclave Engineers Group, Erie, Pennsylvania, USA) with baffles, stirrer, a sparger, a reflux condenser, and a decanter. The autoclave was heated by circulated hot oil. A chiller was used to supply cooling water to the condenser at 2−3 °C to minimise organic chemical loss from the reactor. The air was supplied to the reactor from a cylinder. A computer with a software package (wizcon) was used to monitor the stirrer speed, reactor temperature, and pressure.

The oxidation tests, duration 8 h, with the autoclave reactor were carried out with 600 cm^3 of reaction mixture and 2.0 g of CHRISS catalyst and an air flow rate of 800 cm^3 min^{-1}. The temperature was varied between 130 and 120 °C; the agitator speed was varied from 600 to 300 rpm, and the pressure was varied from 2.0 to 3.0 bar. Each test used fresh feed and catalyst, and the reactor was cleaned prior to each test.

3.3. Dehydrants, Dehydration Processes, and the Dehydration Units. For the proposed dehydration processes the dehydration medium should meet the following requirements: (1) not react chemically with the catalysts, organic reactants, and products, (2) be easily separated from the organic phase, (3) provide the maximum practical extent of water removal, and (4) be economically feasible (e.g. molecular sieves are cheap and can be regenerated). Three dehydrants were tested: 98% sulphuric acid, 1.7−2.4 mm and 2.4−4.5 mm bead 3 Å molecular sieves (theoretical water adsorption capacity 21%), and 2−5 mm granulated self-indicating silica gel (water adsorption capacity 28.5%).[15]

Two dehydration strategies were tested: (1) dehydration of the condensed organic phase from the Dean−Stark trap and (2) direct dehydration of the whole reaction mixture. Figure 2 shows a schematic of the reaction system with the dehydration unit, used in conjunction with a Dean−Stark trap. Using a Dean−Stark trap (or equipment operating on the same principle) alone, condensed water is separated and removed, while the condensed organic phase, *that has a water concentration equal to its equilibrium solubility*, flows back to the reactor directly. Thus, the water concentration in the reaction mixture is approximately *equal to* its equilibrium solubility at the reaction temperature.

However, using the dehydration unit after the Dean−Stark trap (Figure 2), the condensed organic phase is further dehydrated before it flows back to the reactor. Thus, the water concentration in the reaction mixture is *less than* its equilibrium solubility at the reaction temperature.

The dehydration unit consisted of a glass column (internal diameter 48 mm, height 350 mm) filled with 500 cm^3 dehydrant: either molecular sieves (360 g) or silica gel (395 g). The molecular sieves were thermally activated at 250 °C and the silica gel thermally activated at 150 °C before testing. Before each oxidation test, 250 cm^3 of ethylbenzene was added to the glass column to fill the porous space. The working temperature of the dehydration unit was ambient, at approximately 20 °C.

With the sulphuric acid as the dehydrant, the glass column was filled with glass balls to decrease the volume of the sulphuric acid and improve mass transfer. With this dehydration unit, the condensed aromatic phase entered the bottom of the column and dispersed into small drops in the sulphuric acid. The sulphuric acid and aromatics were separated into two layers due to their density difference, with sulphuric acid at the bottom. The dehydrated ethylbenzene top layer then flowed back to the reactor.

For the catalytic oxidation of ethylbenzene at 130 °C and ambient pressure, the condensed organic phase consisted mainly of ethylbenzene due to its lower boiling point, relative to those ofthe products (136 °C for ethylbenzene, 202 °C for acetophenone and 249 °C for benzoic acid).

To dehydrate the reaction mixture, a stream is continuously pumped from the reactor, through a filter, to retain the solid catalyst particles in the reactor, to the dehydration unit, and back to the reactor. In the absence of catalyst and an air supply to the dehydration unit, and with a working temperature in the dehydration unit of approximately 20 °C, it is assumed that no ethylbenzene oxidation occurs in the dehydration unit (i.e., all oxidation products were produced in the reactor). In this case, the dehydration unit consisted of a glass column filled with 500 cm^3 of dehydrant, which could be used for several 24-h runs until the dehydrant was saturated with water. For the first 24-h run, 320 cm^3 of

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(15) Sigma−Aldrich: *Mineral adsorbents, filter agents and drying agents*; Aldrich Technical Information Bulletin Number AL-143.

Table 1. **Aerial oxidation of ethylbenzene with dehydration of condensed organic phase (24 h)**

test	catalyst (CHRISS)	dehydration unit	conversion to acetophenone (%)	conversion to benzoic acid (%)	total conversion (%)	increase of total conversion (%)
1	without	without	43.1	2.6	45.7	−
2	with	without	48.7	6.7	55.4	9.7
3[a]	with	with	53.4	6.8	60.1	14.4
4[b]	with	with	54.2	7.8	62.0	16.3
5[c]	with	with	53.2	7.4	60.5	14.8

[a] Test 3 used 500 cm^3 (360 g) 2.4−4.5 mm bead 3 Å molecular sieves (water adsorption capacity 21%) as dehydrant. [b] Test 4 used 500 cm^3 (360 g) 1.7−2.4 mm bead 3 Å molecular sieves (water adsorption capacity 21%) as dehydrant. [c] Test 5 used 500 cm^3 (395 g) 2−5 mm granulated self-indicating silica gel (water adsorption capacity 28.5%) as dehydrant.

ethylbenzene was added to the glass column, and about 250 cm^3 of liquid was removed at the end (i.e. 70 cm^3 of liquid was adsorbed by the dehydrants). For subsequent 24-h runs, 250 cm^3 of ethylbenzene was added to the glass column at the start, and approximately the same volume of liquid was removed.

In the following discussion the conversion is calculated as $(P_1 + P_2)/(W_1 + W_2)$, where P_1 and W_1 are the product weight and total liquid weight in the reactor respectively, W_2 is weight of the free flow liquid in the dehydration unit, and P_2 is the product weight in the free flow liquid. It should be pointed out that there are products adsorbed in the dehydrants, which are not included in the calculation as direct analysis of the amount was not possible.

4. Results and Discussions

4.1. Dehydration of the Condensed Organic Phase. Sulphuric acid (H_2SO_4) (98%) was used in preliminary test because it does not chemically react with ethylbenzene at lower temperatures, it can be easily separated from the aromatics due to the density difference, and it is an effective dehydrant. In this test, only a small quantity of acetophenone was produced in the first hour, with no further subsequent production detected. In addition, white polymer gel flocculation and flashing metal crystals were observed in the reactor. The low yields of acetophenone are believed to be due to dissolution of sulphuric acid into the ethylbenzene reaction mixture which quickly destroyed the catalyst at 130 °C.

Molecular Sieves and Silica Gel as Dehydrants. Table 1 summarises one set of typical results of the oxidation of ethylbenzene under different conditions of operation using CHRISS catalyst. Each test was carried out for a period of 24 h, with fresh reactants used in each case. Test 1 was operated *without* catalyst and the dehydration unit. Test 2 was operated *with* catalyst but *without* the dehydration unit. Tests 3 and 4 were operated *with* catalyst and the dehydration unit; 2.4−4.5 mm bead 3 Å molecular sieves were used for test 3, and 1.7−2.4 mm bead 3 Å molecular sieves were used for test 4.

With the catalyst, the conversion to acetophenone and benzoic acid was increased from 45.7 to 55.4% (w/w). With the catalyst and dehydration unit, the conversion to acetophenone and benzoic acid was further increased to 62.0% (w/w). Table 1 shows that about 32% (test 3) to 40% (test 4) improvement of the total conversion was due to the dehydration process.

In tests 3 and 4 there is only a marginal difference in product yield with two different sizes of dehydrant, with the smaller-size molecular sieves giving slightly higher conversion. This may be due to faster water adsorption obtained with larger solid/liquid surface area of the smaller-size dehydrant.

The use of 2−5 mm of granulated self-indicating silica gel as dehydrant produced results similar to those obtained with molecular sieves (test 5 in Table 1). The conversion to acetophenone and benzoic acid were 53.2 and 7.4% respectively.

4.2. Dehydration and the Induction Period. Previous work[1] on the catalytic oxidation of ethylbenzene with the dichromate/alumina catalyst EPAD has shown that there is a long induction period, of some 2 to 3 h, before significant reaction proceeds. This induction period is believed to be associated with initial hydration of catalyst during storage, that is, the hydrophilic alumina support adsorbs moisture from air during storage. Due to the porous structure and hydrophilicity of alumina, the unfavourable capillary action makes it difficult for the adsorbed water to escape and for the reactant to reach the Cr cation sites inside the meso-pores, during the initial stages of reaction.

Previous work[2] has also shown that a shorter induction period and a higher conversion rate were obtained with the chromium/silica catalyst CHRISS than with the alumina-based catalyst. One reason for this may be due to the larger pore size (100 Å of the silica supports compared with 20 Å of the alumina supports), which leads to a lower capillary rise and easier removal of water from the meso-pores.

To eliminate the induction period the catalyst was dried at 110 °C overnight before use in the oxidation process. Figure 3 gives a typical example of the oxidation of ethylbenzene with the predried chromium/silica catalyst using the dehydration unit (silica gel, dehydration of condensed organic phase). As can be seen there was a steady rise in the acetophenone concentration with time, and no induction period was observed.

4.3. Dehydration of the Reaction Mixture. Table 2 shows the results obtained for the direct dehydration of the ethylbenzene reaction mixture with 3 Å molecular sieves and 2−5 mm granulated self-indicating silica gel, using the small glass reactor.

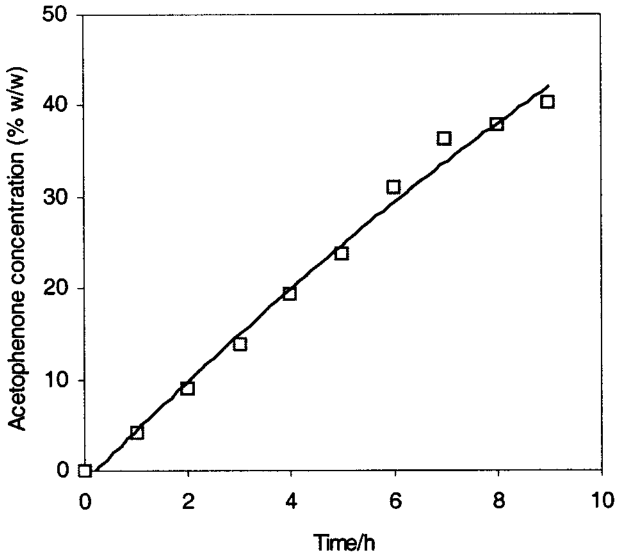

Figure 3. **Physical dehydration.**

The test with silica gel used the same dehydration column for four 24-h runs. Each run used the same amount of fresh ethylbenzene and catalyst. The conversion rates increased with the use of dehydrant in the column and particularly after the second run. This effect is due to adsorption of oxidation products by the silica gel during run 1. The amounts of product adsorbed during subsequent runs were thus reduced.

Overall, by using the silica gel as dehydrant the conversion of ethylbenzene was increased by approximately 6%, compared with no dehydrant.

Table 2 also shows the results obtained with molecular sieves as dehydrant. The average conversion of ethylbenzene of two runs was 37.5%, compared with 41.3% with no dehydrant. The result differed from that obtained when the molecular sieves were used for dehydration of condensed organic phase, where positive improvement of the conversion rate was observed. The difference in behaviour is believed, in part, to be due to the fact that in dehydrating the condensed organic phase, only the reactant ethylbenzene goes through the dehydration unit, whereas in dehydrating the reaction mixture, the whole reaction liquid goes through the dehydration unit. In addition, compared with silica gel, the difference in performance using molecular sieves in both dehydration systems may be due to the outer surface of the molecular sieves or the binder material chemically reacting with, or physically adsorbing the intermediate radicals of the background oxidation.

4.4. Effect of the Background Oxidation of Ethylbenzene. For the aerial oxidation of ethylbenzene, without catalyst and the dehydration unit, a conversion of 45.7% was obtained after 24 h of operation (test 1 in Table 1). This background oxidation might be from small quantities of organic peroxides, present in ethylbenzene as impurities.[1] With catalyst, the apparent total conversion is therefore the sum obtained via two different reaction mechanisms: background oxidation and catalytic oxidation.

Dehydration of the reaction mixture may lead to two opposite effects: adsorption of water from the mixture, which assists catalyst performance, and the dehydrants may chemically react with, or physically adsorb the intermediate radicals of the background oxidation, which will decrease the rate of the background oxidation, and hence decrease the apparent conversion rate.

Oxidation carried out without dehydration using alumina- and silica-supported catalysts give some support to the second effect. Figure 4 shows that for the oxidation of ethylbenzene with a Cr/alumina catalyst (EPAD), when the quantity of catalyst was increased from 1.0 to 5.0 g, the induction period increased, indicating a greater amount of catalyst support may inhibit the oxidation. Also, using an unmodified alumina support in place of the Cr/alumina catalyst, a conversion of 13.4% was obtained after 24-h of operation, demonstrating that the alumina support (Al_2O_3) inhibits the inherent background oxidation. In previous research, alumina has been used as a stationary phase in column chromatography to remove organic peroxides effectively.[16] Thus, circulating the reaction mixture through the dehydration unit could decrease the intermediate organic radicals in the substrate, thus decreasing the level of the background oxidation.

Figure 5 shows that, for the oxidation of ethylbenzene with the Cr/silica catalyst (CHRISS), when the quantity of catalyst was increased, from 1.0 to 5.0 g, the induction period increased, which suggests that silica also adsorbs the intermediate organic radicals, but not as significantly as alumina (Figure 4). This behaviour gives some support to the superior performance achieved with silica gel as dehydrant (Table 2) compared with the use of molecular sieves.

4.5. Effect of Circulation Rate of the Reaction Mixture. One advantage of direct dehydration of the reaction mixture is that the flow rate of the organic phase can be controlled. Two sets of tests were carried out, with identical experimental conditions, to assess the effect of the organic phase circulation rates. In each set, the same silica gel dehydration column was used for three 24-h runs, and each run used the same amount of fresh ethylbenzene and catalyst. Table 3 shows the results of the tests where a higher circulation rate gave a slightly lower average conversion rate, although there is an indication that, at least in the final test, a higher flow rate may be beneficial.

Overall there is only a small influence of flow rate on the conversion of ethylbenzene, with an indication of an improvement in performance, at higher flow rate, due to a possible improvement in mass transfer of the dehydration process.

Increasing the circulation rate, during dehydration of the reaction mixture, could improve the mass transfer condition in the dehydration unit, which could, on one hand, increase the dehydration rate, and hence the apparent conversion rate, and on the other hand, increase adsorption of the intermediate organic radicals, which could decrease the rate of the background oxidation.

4.6. Reaction with a Continuous Temperature Increase. For the oxidation processes with both EPAD and CHRISS, the reaction rates were quite low, typically, at 130 °C, approximately 50% of ethylbenzene was converted in 24 h. Thus, it might be possible to exploit the difference in

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(16) Eggersgluss, W. *Organische Peroxyde*; Monographieran zu Angewandte Chemie, No. 61; Verlag Chemie: Weinheim, 1951.

Table 2. **Aerial oxidation of ethylbenzene with direct dehydration of the whole reaction mixture (24 h run)**

dehydrant	test[a]	conversion to acetophenone (%)	conversion to benzoic acid (%)	conversion of acetophone and benzoic acid (%)
molecular sieves[b]	run 1	33.5	3.6	37.1
	run 2	33.9	4.0	37.9
no dehydrant	run 1	37.5	3.7	41.3
silica gel[c]	run 1	38.4	4.6	43.0
	run 2	42.1	4.7	46.7
	run 3	42.2	4.9	47.1

[a] Fresh CHRISS catalyst and ethylbenzene were used for each 24-h run. [b] The same 500 cm^3 (360 g) 1.7–2.4 mm bead 3 Å molecular sieves (water adsorption capacity 21%) was used as dehydrant for two 24-h runs. [c] The same 500 cm^3 (395 g) 2–5 mm granulated self-indicating silica gel (water adsorption capacity 28.5%) was used as dehydrant for four 24-h runs.

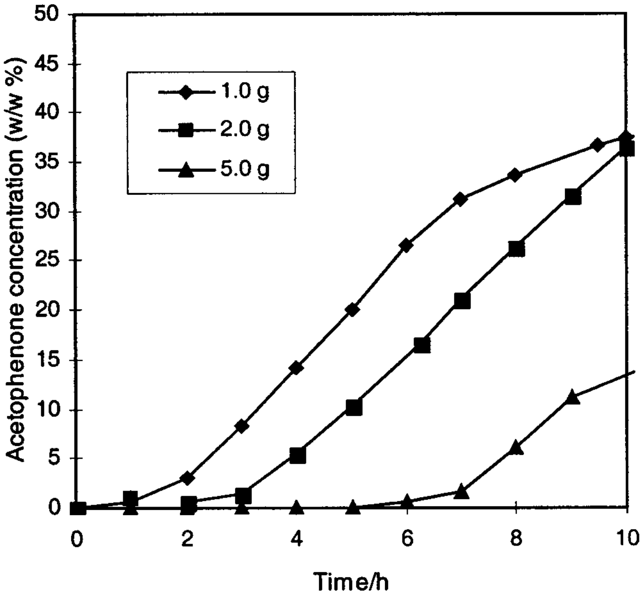

Figure 4. **Oxidation of ethylbenzene with Cr/alumina catalyst.**

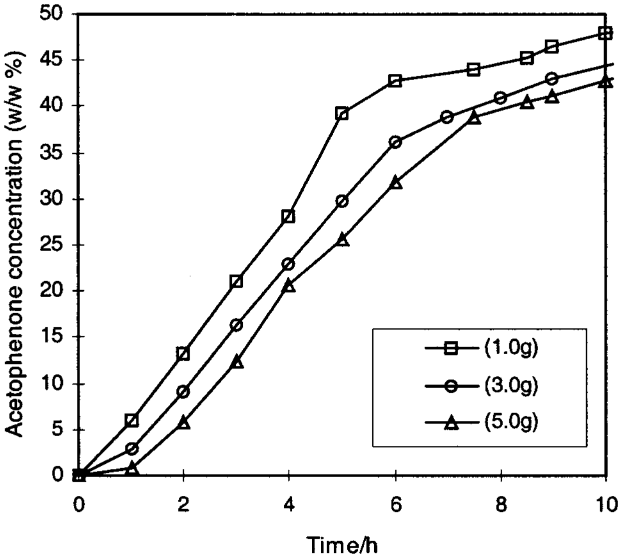

Figure 5. **Oxidation of ethylbenzene with Cr/silica catalyst.**

Table 3. **Effect of the circulation rate on the oxidation of ethylbenzene with dehydration of the reaction mixture**

flow rate	2.6 mL/min	7.5 mL/min
run 1	43.0%	36.3%
run 2	46.7%	45.5%
run 3	46.6%	49.3%
average	45.4%	43.7%

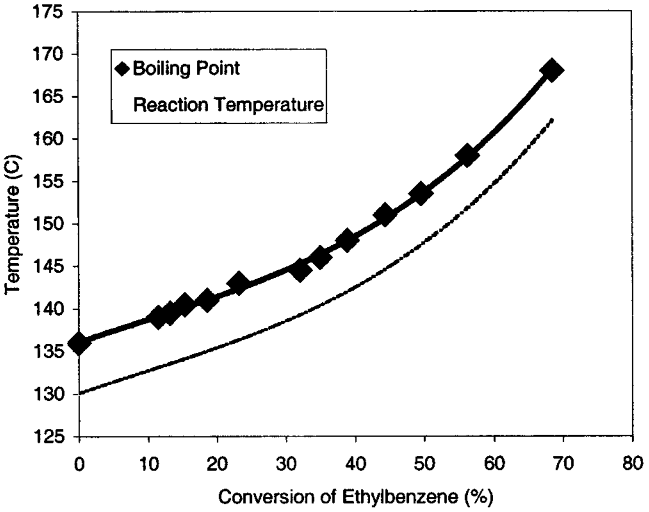

Figure 6. **Boiling point of reaction mixture.**

the boiling points of ethylbenzene, acetophenone, and benzoic acid (at atmospheric pressure 136, 202, and 249 °C, respectively) and operate at higher temperatures. Thus, as the boiling point of the reaction mixture increases with conversion of ethylbenzene, for example, from 136 to 168 °C at a conversion of 68.5% (Figure 6), it is possible to continuously increase the reaction temperature during the oxidation. Ideally, the reaction temperature would be controlled some 5–6 °C below the boiling points during the oxidation process (dashed line in Figure 6).

The experimental procedure adopted was to use temperature step increases (0–3 h at 130 °C, 3–6 h at 135 °C, 6–9 h at 140 °C, and 9–24 h at 145 °C) for the oxidation of ethylbenzene with Cr/Silica catalyst, but without the dehydration unit. Figure 7 shows the experimental results, where the 24 h conversion obtained was 68.5%, which compared favourably with the conversion of 55.4% with a constant temperature at 130 °C.

The experiment with temperature steps was repeated using the dehydration unit (silica gel). The 24 h conversion obtained was 68.2% which whencompared to the conversion of 68.5% without the dehydration unit, showed that dehydration did not improve the reaction performance when the reaction was carried out at increased temperature. One explanation for this is that, at higher reaction temperature

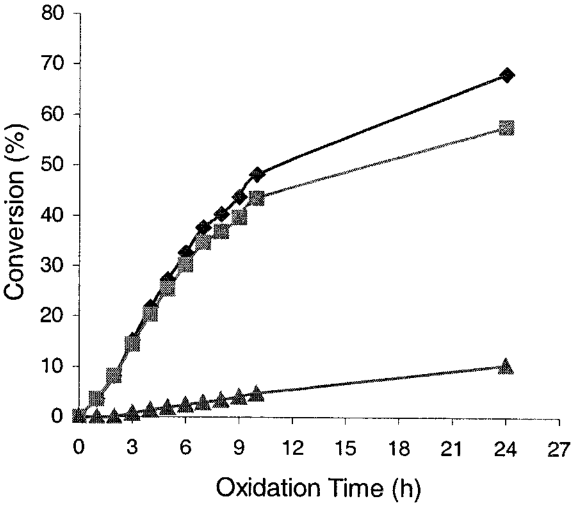

Figure 7. **Oxidation of ethylbenzene with increasing temperature steps. (▲) Benzoic acid, (■) acetophenone, (◆) acetophenone and benzoic acid.**

(above 140 °C), the mass transfer rate of water from Cr cation sites is higher than the rate of production of water by reaction, and therefore water mass transfer is no longer a control barrier of the process. Previous research has reported that the loss of water from silica gel may begin at 50 °C, reaching a maximum rate of desorption at about 140 °C. [12]

5. Conclusions

For the catalytic oxidation of ethylbenzene to acetophenone, investigation of the influence of dehydration has shown that: (1) 98% sulphuric acid is not a suitable dehydrant for the proposed dehydration processes due to destruction of the catalyst, (2) the molecular sieves and silica gel are suitable dehydrants for the process dehydrating the condensed organic phase, and (3) silica gel is a suitable dehydrant for the process of dehydrating the reaction mixture. Overall, selection of a suitable dehydrant is the key in the dehydration process.

By operating the reactor with an increase in reaction temperature, better performance is achieved than under isothermal conditions (at atmospheric pressure). With silica-supported catalysts, the dehydration process cannot improve the reaction performance under conditions of increased reaction temperature.

The advantages of dehydrating the condensed organic phase, as opposed to dehydrating the reaction mixture, are:

(1) no filter is needed as the solid catalyst particles remain in the reactor, and

(2) no pump is needed as, with a suitable hydraulic arrangement, the condensed organic phase will flow back to the reactor due to gravity.

The main shortcoming in dehydrating the condensed organic phase is that the flow rate of the organic phase is controlled by the rate of condensation.

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