# Autooxidation of cumene catalyzed by transition metal compounds on polymeric supports

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## Abstract

The autooxidation of cumene to cumene hydroperoxide (CHP) in the presence of a supported catalyst was investigated. When Cu(OAc)$_2$ was supported on Chelex, polyvinylpyridine or SiO$_2$, it was demonstrated that polyvinylpyridine and SiO$_2$ are poor supports for a catalyst in cumene autooxidation. Several metal ions supported on Chelex were tested for their effectiveness in initiating cumene autooxidation at 353 K. The rate of autooxidation follows the order Mn(II) > Cu(II) > Co(II) > Ni(II) > Fe(II). However, Mn(II) gives a poor selectivity to CHP as it can also catalyze the conversion of CHP to 2-phenyl-2-propanol. The most suitable catalyst in the steady propagation of cumene autooxidation has the composition of Cu(OAc)$_2$ (0.6 mmol) on dried Chelex (1.0 g), denoted Cu(OAc)$_2$–CHX-0.6. There is an optimal ratio of Cu(OAc)$_2$–CHX-0.6 to substrate (0.2 g per 10 ml cumene) to achieve an autooxidation rate that is 63% greater than that initiated with CHP at 353 K. The selectivity to CHP is also greater. This ratio is also the best for the rate of initiation in cumene autooxidation to CHP. The lifetime of this catalyst is long; no sign of deactivation was observed in our experiments.

## 1. Introduction

The oxidation of hydrocarbons with oxygen or air as oxidant is an important industrial process in the manufacture of commodity chemicals [1]. This oxidation in the presence of a transition-metal catalyst in both homogeneous and heterogeneous systems, has been extensively studied [2–5]. Cumene oxidation is one such important process of oxidation with dioxygen. Cumene is oxidized through a free-radical reaction pathway to cumene hydroperoxide (CHP) which is a precursor to phenol and acetone in the Hock process. In the industrial process, CHP itself serves as initiator [6]. A homogeneous catalyst M(Nf)$_2$ (Nf = naphthenate, M = Zn, Cd) [7] and a heterogeneous catalyst (Ag, Cu or Pt on support) [8] do not improve the yield or selectivity to CHP. In most cases, the selectivity to CHP deteriorated in the presence of these catalysts.

In this work, we attempted to enhance the rate of autooxidation of cumene using a supported transition-metal catalyst which potentially possesses the desired advantages of a homogeneous catalyst with high selectivity in mild reaction conditions and a heterogeneous catalyst in the ease of isolation of product. We found that a particular combination of metal salt and support can enhance the rate of autooxidation by 63% relative to that

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initiated by CHP. Furthermore, the selectivity is also improved with this catalyst.

## 2. Experimental

### 2.1. Material and equipment

Ion exchange resin Chelex 100, which is a styrene divinylbenzene copolymer containing paired iminodiacetate ions, was purchased from Bio-Rad. This resin has a high affinity to metal ions in the + 2 oxidation state. It is not stable above 373 K. Poly-4-vinylpyridine (2% cross linking) and cumene were purchased from Aldrich. Silica gel 60 (70-230 mesh) was obtained from Merck Cumene was purified by repeated reaction with concentrated sulfuric acid until the acid layer was colorless. It was then washed with $H_2O$, neutralized with sodium carbonate and washed with $H_2O$ again. After being dried over $MgSO_4$ and refluxed over $CaH_2$, cumene was distilled just before use.

$^1$H NMR spectra were recorded on a Gemini-300 spectrometer. The metal contents of supported catalyst were measured on a Kontron Plasmakon Model S-35 ICP instrument. IR spectra were obtained on a JASCO 300E FTIR spectrometer. GC analysis were performed on a Shimadzu 8A gas chromatographic instrument with a flame ionization detector.

### 2.2. Synthesis of supported catalyst

Chelex 100 (which contained about 75% water as purchased) was dried in a vacuum oven at 323 K to a constant mass. The dry Chelex was suspended in water and the metal salt to be impregnated was then added. After stirring for 1 h, methanol was added and stirring was continued for 30 min. After filtering and drying in a vacuum oven, the supported catalyst was obtained. The catalyst is denoted MS-CHX-r, in which MS represents metal salt, CHX represents the Chelex support and r is the amount of metal salt in mmol per gram of support.

The procedure of synthesizing the catalyst supported on polyvinylpyridine (PVP) is described below. PVP (1.0 g) was added to a methanol solution (10 ml) of a metal salt (0.6 mmol). Methanol was added to make the total volume 50 ml. After stirring for 24 h, the catalyst was obtained by filtration, followed by washing with water and acetone, and drying in a vacuum oven. This catalyst is denoted as MS-PVP-0.6.

The silica supported catalyst was prepared according to the literature method [9]. The metal content is 0.6 mmol per gram of support. It is denoted $MS-SiO_2-0.6$.

### 2.3. Oxidation of cumene

Oxidation of cumene was carried out in a closed system made of Pyrex glassware which can be connected to vacuum line and oxygen source by way of stopcocks. The system consists of a water jacketed oxygen reservoir including a condenser, and a 25 ml flask connected to the condenser. The procedure of the oxidation reaction is described below. Cumene (10 ml) with catalyst was placed inside the flask, degassed three times by the freeze-pump-thaw cycle. Then oxygen was introduced at the desired pressure. The oxidation reactions were carried out between 333-363 K by heating the cumene solution. The temperature of the gas in the small volume between the cumene and the thermostated (298 K) oxygen reservoir (0.11 l) could not be defined. However, this uncertainty was circumvented by a calibration procedure that consisted of measuring before and after the cumene was heated in the absence of catalyst or initiator (to avoid oxidation). The oxygen pressure was monitored with a Atsuryu PT-15PV pressure transducer interfaced to a PC. Product analyses were performed with both GC and $^1$H NMR spectroscopy. In GC analysis, iodobenzene was used as internal standard. At the conditions of $N_2$ flow rate 20 ml/min, at 413 K, besides starting cumene, CHP, 2-phenyl-2-propanol (PP) and acetophenone (AP) were the only products ever detected on comparison with the retention times of pure samples. In $^1$H NMR anal-

yses, the reaction mixtures (after filtering away the catalyst) were dissolved in $CDCl_3$ with internal standard of methanol for quantitative analysis and TMS for chemical shift measurement. From the methyl region, cumene ($\delta$ 1.15 ppm, d), CHP ($\delta$ 1.49 ppm, s), 2-phenyl-2-propanol ($\delta$ 1.45 ppm, s) and acetophenone ($\delta$ 2.30 ppm, s) were identified as the only possible products in the oxidation reaction. From the integrated area, by comparison with that of the internal standard of methanol, the concentrations of the products were deduced. To measure the amount of CHP accurately, a standard iodometric titration method [10] was employed.

## 3. Results and discussion

In the presence or absence of supported catalyst, cumene oxidation by $O_2$ to cumene hydroperoxide (CHP) was investigated by monitoring the $O_2$ pressure, $P(O_2)$, in a closed system. As shown in Fig. 1, at 353 K , pure cumene is oxidized by $O_2$ only after a long induction period ( $\approx 5$ h) which is indicative of a free radical reaction pathway. In the presence of CHP, rapid $O_2$ consumption was observed. The $O_2$ consumption slowed at an $O_2$

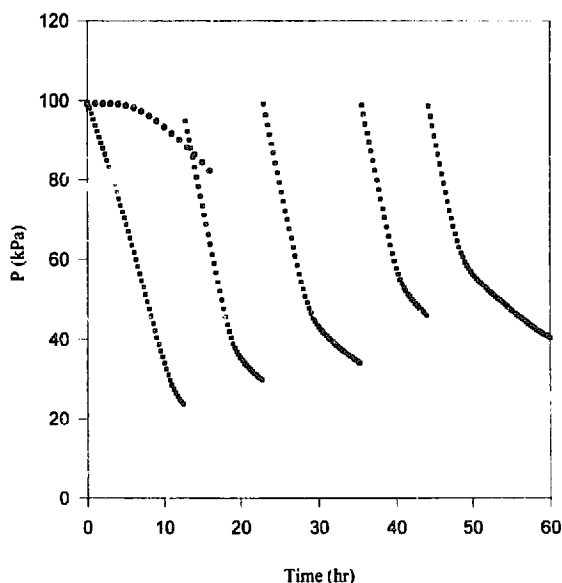Fig. 1. $P(O_2)$ in a closed system as a function of time for autooxidation of cumene ( 10 mL) at 353 K (●): pure cumene, (■) with cumene hydroperoxide (0.64 g) as initiator and with repetitive admission of fresh $O_2$.
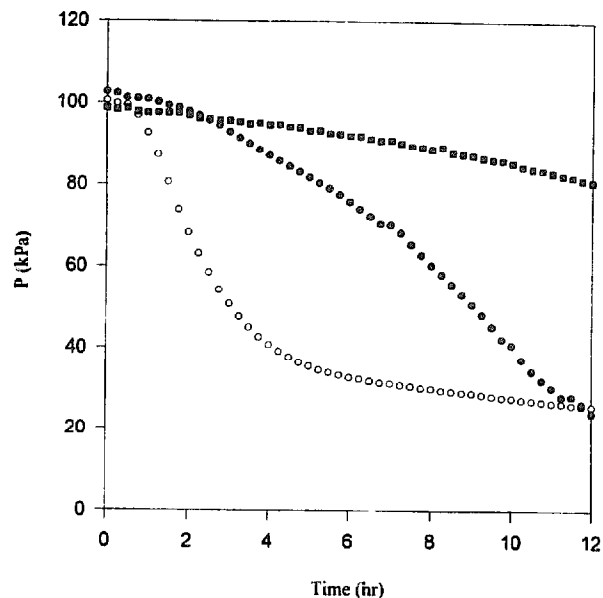
Fig. 2. $P(O_2)$ as a function of reaction time in autooxidation of cumene (10 ml) in the presence of catalyst (0.2 g): (●): $Cu(OAc)_2$-CHX-0.6, (○): $Cu(OAc)_2$-PVP-0.6 and (■): $Cu(OAc)_2$-SiO$_2$-0.6.

pressure ca. 26.7 kPa. When fresh $O_2$ was introduced into the reaction solution, rapid consumption was again observed. This process was repeated several times. When the conversion of cumene was 22%, analysis of the products indicated that the selectivity to CHP is 92.1%. The side products were 2-phenyl-2-propanol PP (7.0%) and acetophenone AP (0.9%).

### 3.1. Support effect

When the autooxidation of cumene (10 ml) was carried out in the presence of supported catalysts (0.2 g), $Cu(OAc)_2$-CHX-0.6, $Cu(OAc)_2$-PVP-0.6 or $Cu(OAc)_2$-SiO$_2$-0.6, oxygen was consumed as shown in Fig. 2. The relative rates of oxygen consumption for the three catalysts with the same metal content are $Cu(OAc)_2$-PVP-0.6 $\gg$ $Cu(OAc)_2$-CHX-0.6 $\gg$ $Cu(OAc)_2$-SiO$_2$-0.6. The differences among these catalysts also show in the distributions of products, collected in Table 1. After reaction for 12 h with reaction conditions 353 K, cumene (10 ml), catalyst (0.2 g), initial $O_2$ pressure (93.3 kPa), the oxidation of cumene catalyzed with $Cu(OAc)_2$-CHX-0.6 resulted in a CHP selectivity of 99.4%, whereas

Table 1

Product distribution of the autooxidation of cumene (10 ml) in the presence of catalyst (0.2 g) for 12 h at 353 K; initial $P(O_2)$ is 93.3 kPa

| Catalyst | $\alpha$ [a] (%) | $\Delta n(O_2)$ [b] (mmol) | CHP [c] (mmol) | PP [d] | AP [e] | S(CHP) [f] (%) |
|---|---|---|---|---|---|---|
| Cu(OAc)₂– CHX-0.6 | 5.36 | 3.83 | 3.80 | 0.03 | 0 | 99.4 |
| Cu(OAc)₂– PVP-0.6 | 1.08 | 3.71 | 0.43 | 0.34 | 0 | 55.8 |
| Cu(OAc)₂– SiO₂-0.6 | 0.97 | 0.69 | 0.28 | 0.33 | 0.08 | 40.6 |

[a] Conversion of cumene.

[b] Amount of oxygen reacted.

[c] CHP denotes cumene hydroperoxide, determined by iodometric method.

[d] PP denotes 2-phenyl-2-propanol, analyzed by $^1$H NMR.

[e] AP denotes acetophenone, determined by GC.
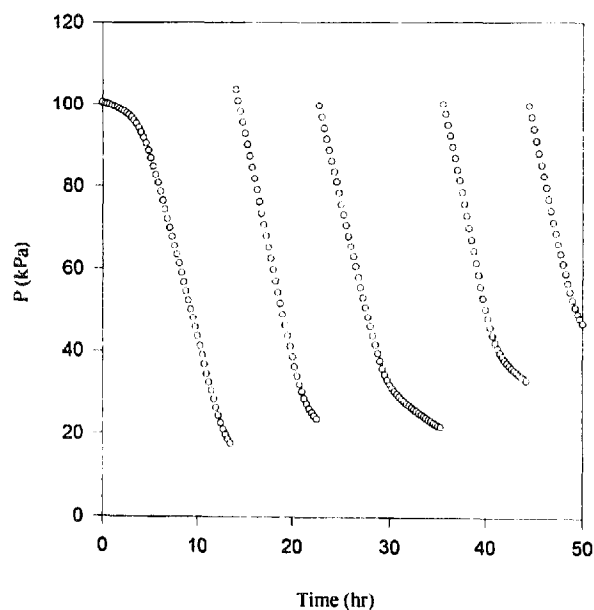
[f] S(CHP) denotes selectivity to CHP relative to cumene.



Fig. 3. $P(O_2)$ as a function of reaction time in autooxidation of cumene (10 ml) in the presence of Cu(OAc)₂–CHX-0.6 (0.2 g) at 353 K with repeated introduction of fresh $O_2$.

with the catalysts Cu(OAc)₂–PVP-0.6 and Cu(OAc)₂–SiO₂-0.6, the selectivities were 55.6 and 40.6% respectively. With Cu(OAc)₂–PVP-0.6 catalyst, the total number of moles of CHP and PP is only 21% of the number of moles of $O_2$ reacted. Another oxygen sink was not detected in the products by GC and $^1$H NMR spectroscopy. IR analysis of the spent and fresh Cu(OAc)₂–PVP-0.6 catalyst indicates extra IR peaks in the

region 1150–1300 cm$^{-1}$. These extra peaks are similar to those of pyridine N-oxide [11] which is also the most likely oxidation product in this system. Therefore, oxidation of PVP appears to be the major sink of oxygen in Cu(OAc)₂–PVP-0.6 catalyzed autooxidation of cumene. When Cu(OAc)₂–SiO₂-0.6 is the catalyst, the poor selectivity to CHP is consistent with the literature report [12] that SiO₂ can catalyze the conversion of CHP to 2-phenyl-2-propanol and acetophenone. The small catalytic activities and poor selectivities toward CHP in cumene autooxidation catalyzed by Cu(OAc)₂–PVP-0.6 and Cu(OAc)₂–SiO₂-0.6 indicate that PVP and SiO₂ cannot serve as suitable supports for the autooxidation of cumene to CHP.

### 3.2. Stability of Cu(OAc)₂–CHX-0.6 catalyst

The life time of Cu(OAc)₂–CHX-0.6 catalyst was further tested by repetitive admission of fresh $O_2$. As shown in Fig. 3, in the first run, when $O_2$ pressure reached 13.3 kPa, the rate of oxidation slowed down. In the succeeding runs, the slow-down pressure, $P_s$, increased. However, the rates of oxygen consumption for pressure reaching greater than $P_s$ were identical (1.91 × 10$^{-5}$ M/ sec ) except in the first run that included an induction period. At the end of the tenth run, the conversion is 40% with a selectivity to CHP 96% that is less than 99.4% for a single run (Table 1). On the other hand, this selectivity is much better than that initiated with CHP at 22% conversion (92.1%). When fresh cumene was used in the presence of the spent Cu(OAc)₂–CHX-0.6 catalyst, exactly the same curves for oxygen consumption as in Fig. 3 including the induction period, were obtained. Therefore, the life time of Cu(OAc)₂–CHX-0.6 is extremely long. The reaction pattern of cumene oxidation in Fig. 3 is very similar to that initiated with CHP in Fig. 1 except the induction period. The effect of catalyst in the induction period and during the steady propagation period warrant further investigation.
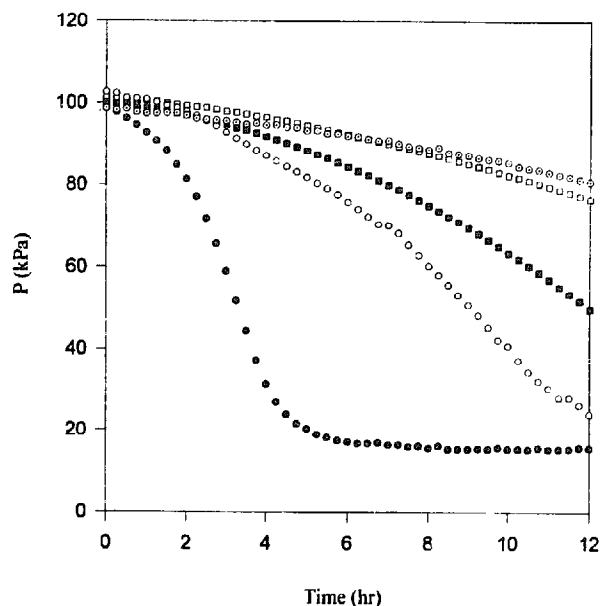
Fig. 4. $P(O_2)$ as a function of reaction time in autooxidation of cumene (10 ml) in the presence of catalyst (0.2 g): (●): Mn(OAc)$_2$-CHX-0.6, (○): Cu(OAc)$_2$-CHX-0.6, (■): Co(OAc)$_2$-CHX-0.6, (□): Ni(OAc)$_2$-CHX-0.6, and (◉): FeCl$_2$-CHX-0.6.

Table 2
Product distribution of the autooxidation of cumene (10 ml) in the presence of catalyst (0.2 g) for 12 h at 353 K, initial $P(O_2)$ is 93.3 kPa. All notations are specified in Table 1

| Catalyst | $\alpha$ (%) | $\Delta n(O_2)$ (mmol) | CHP (mmol) | PP | S(CHP) (%) |
|---|---|---|---|---|---|
| Mn(OAc)$_2$-CHX-0.6 | 5.10 | 3.65 | 3.39 | 0.26 | 92.9 |
| Cu(OAc)$_2$-CHX-0.6 | 5.36 | 3.83 | 3.80 | 0.03 | 99.4 |
| Co(OAc)$_2$-CHX-0.6 | 3.79 | 2.71 | 2.70 | 0.01 | 99.6 |
| Ni(OAc)$_2$-CHX-0.6 | 2.27 | 1.62 | 1.60 | 0.02 | 99.0 |
| FeCl$_2$-CHX-0.6 | 1.24 | 0.89 | 0.88 | 0.01 | 99.0 |

Table 3
Product distribution of autooxidation of cumene (10 ml) in the presence of various amounts of Cu(OAc)$_2$-CHX-0.6 catalyst for 12 h at 353 K, initial $P(O_2)$ is 93.3 kPa. All notations are specified in Table 1

| Amount of catalyst (g) | $\alpha$ (%) | $\Delta n(O_2)$ (mmol) | CHP (mmol) | PP | S(CHP) (%) | $\alpha'$ [a] |
|---|---|---|---|---|---|---|
| 0.1 | 3.87 | 2.77 | 2.75 | 0.02 | 99.3 | 38.7 |
| 0.2 | 5.36 | 3.83 | 3.80 | 0.03 | 99.4 | 26.8 |
| 0.4 | 2.90 | 2.07 | 2.05 | 0.02 | 99.0 | 7.25 |
| 0.6 | 2.59 | 1.85 | 1.84 | 0.01 | 99.2 | 4.31 |

[a] $\alpha'$ is the conversion per unit mass (g) of Cu(OAc)$_2$-CHX-0.6 catalyst in cumene (10 ml).

## 3.3. Effect of metal and temperature on the induction period of MS-CHX-0.6 catalyzed cumene oxidation

Catalysts of various metal salts adsorbed onto Chelex 100 with the same of moles per gram of support were investigated under identical reaction conditions 353 K and initial $O_2$ pressure 93.3 kPa. The results appear in Fig. 4. The order of the effectiveness of catalysts in initiating the autooxidation reaction is:

$$Mn(II) > Cu(II) > Co(II) > Ni(II) > Fe(II)$$
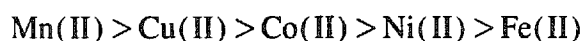
After reaction for 12 h without additional $O_2$, the product distributions were determined (Table 2). Mn(OAc)$_2$-CHX-0.6 has a poor selectivity 92.9% to CHP, whereas other catalysts gave a selectivity 99% or over. The poor selectivity of Mn(OAc)$_2$-CHX-0.6 results form its ability to convert CHP to PP that was observed in an experiment in which CHP was mixed with Mn(OAc)$_2$-CHX-0.6 at 353 K followed by product analysis. According to the rate of initiation and the selectivity to CHP, Cu(OAc)$_2$ supported on Chelex is worthy of further investigation.

When activated with varied amounts of Cu(OAc)$_2$-CHX-0.6, the total amount of oxygen consumed within a reaction period 12 h under identical conditions (353 K, cumene 10 ml and initial $O_2$ pressure 93.3 kPa) varied. As shown in Table 3, a catalyst dose of 0.2 g Cu(OAc)$_2$-CHX-0.6 per 10 ml cumene is optimum. The effect of activation by unit mass of Cu(OAc)$_2$-CHX-0.6, $\alpha'$, shown in column 7 in Table 3 is decreasing monotonically with increasing amount of catalyst.

To understand the reason for the monotonically decreasing effect on increasing the amount of Cu(OAc)$_2$-CHX-0.6, Chelex was added to cumene (10 ml) with Cu(OAc)$_2$-CHX-0.6 (0.2 g). The amounts of oxygen consumed, $\Delta n(O_2)$, in 12 h reaction time at 353 K with initial $O_2$ pressure of 93.3 kPa were 3.83, 2.54, and 1.48 mmol in the presence of Chelex with the amounts 0, 0.05 and 0.10 g, respectively. Therefore, Chelex support itself can retard the rate of initiation. The
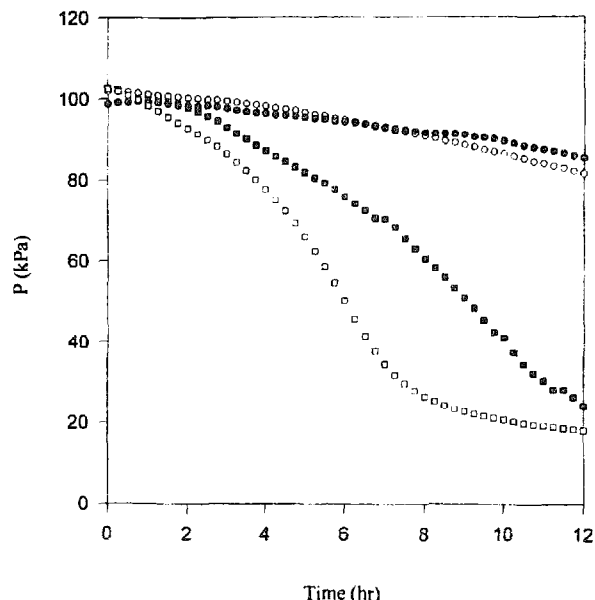
Fig. 5. $P(O_2)$ as a function of reaction time in autooxidation of cumene (10 ml) in the presence of catalyst (0.2 g) at 333 K (●), 343 K (○), 353 K (▨) and 363 K (□).

Table 4
Product distribution of autooxidation of cumene (10 ml) in the presence of catalyst Cu(OAc)$_2$-CHX-0.6 (0.2 g) for 12 h at various temperatures; initial $P(O_2)$: 93.3 kPa. All notations are specified in Table 1

| Temperature (K) | $\alpha$ (%) | $\Delta n(O_2)$ (mmol) | CHP (mmol) | PP | S(CHP) (%) |
|---|---|---|---|---|---|
| 333 | 0.80 | 0.57 | 0.56 | 0.01 | 99.1 |
| 343 | 1.43 | 1.02 | 1.01 | 0.01 | 99.0 |
| 353 | 5.36 | 3.83 | 3.80 | 0.02 | 99.4 |
| 363 | 5.55 | 3.97 | 3.86 | 0.11 | 97.3 |

monotonic decrease of $\alpha'$ with the amount of Cu(OAc)$_2$-CHX-0.6 is explained by the retarding nature of Chelex partially if not completely.

The effect of temperature on the rate of oxidation is shown in Fig. 5. As temperature increased, the rate of oxygen consumption increased. The results of product distribution after reaction for 12 h, are summarized in Table 4. Below 353 K, the selectivity was at least 99%. At 363 K, the selectivity decreased to 97.3%.

### 3.4. Rate of cumene oxidation in the steady propagation state

This steady propagation rate is a critical parameter for economic considerations in industrial

application. This rate was obtained when fresh O$_2$ was repeatedly admitted to the reaction system until a steady value was attained and maintained. A steady rate was usually reached in the second cycle after the first initiation cycle. A typical example is shown in Fig. 3. Besides Cu(OAc)$_2$-CHX-0.6, catalysts with different metal loading, Cu(OAc)$_2$-CHX-0.4 and Cu(OAc)$_2$-CHX-1.0, were also investigated. 1.0 mmol of divalent metal per 1 g of support is the maximum metal loading for Chelex 100. The steady rates of oxygen consumption are given in Table 5. When the amount of Cu(OAc)$_2$-CHX-0.6 increases, the oxygen consumption rate reaches a maximum (0.2 g per 10 ml cumene) then decreases when more Cu(OAc)$_2$-CHX-0.6 is present. This behavior is similar to that observed in the initiation period that there is an optimum amount of catalyst. With varied metal loading, Cu(OAc)$_2$-CHX-0.6 was obviously better than Cu(OAc)$_2$-CHX-0.4 and Cu(OAc)$_2$-CHX-1.0 in terms of per unit amount of Cu(OAc)$_2$. This average optimum rate is 63% greater than the average rate ($1.12 \times 10^{-5}$ M s$^{-1}$) when initiated with CHP.

### 3.5. Mechanism of autooxidation of cumene

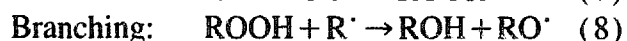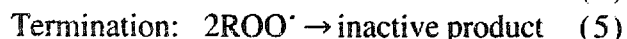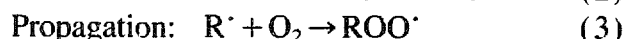The generally accepted mechanism [13–15] of the autooxidation of cumene is given in the scheme below:

Table 5
Rate of autooxidation of cumene (10 ml) in the steady propagation stage in the presence of various amounts of CHP initiator, or various catalysts and their amounts at 353 K

| Catalyst | Weight catalyst (g) | Weight CHP [a] (g) | Rate ($10^{-5}$ M/s) |
|---|---|---|---|
| – | – | 0.10 | 1.03 |
| – | – | 0.30 | 1.06 |
| – | – | 0.64 | 1.27 |
| Cu(OAc)$_2$-CHX-0.6 | 0.1 | 0 | 1.24, 1.32 |
| Cu(OAc)$_2$-CHX-0.6 | 0.2 | 0 | 1.91, 1.84, 1.73 |
| Cu(OAc)$_2$-CHX-0.6 | 0.4 | 0 | 1.26 |
| Cu(OAc)$_2$-CHX-0.6 | 0.6 | 0 | 1.13 |
| Cu(OAc)$_2$-CHX-0.4 | 0.2 | 0 | 0.70 |
| Cu(OAc)$_2$-CHX-1.0 | 0.2 | 0 | 1.30 |

[a] Amount of cumene hydroperoxide initiator.

Initiation:     $RH \rightarrow \rightarrow R^{\cdot}$                                                    (1)

                $ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH$                                           (2)

Propagation:    $R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$                                              (3)

                $ROO^{\cdot} + RH \rightarrow ROOH + {}^{\cdot}R$                                      (4)

Termination:    $2ROO^{\cdot} \rightarrow$ inactive product                                           (5)

                $2R^{\cdot} \rightarrow R_2$                                                           (6)

                $R'^{\cdot} + ROO^{\cdot} \rightarrow ROOR'$                                           (7)

Branching:      $ROOH + R^{\cdot} \rightarrow ROH + RO^{\cdot}$                                        (8)
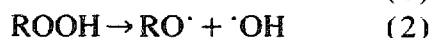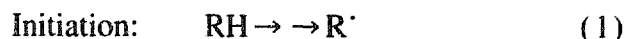
R and R' are cumyl group. In the initiation steps, cumene may go through several different processes to become cumyl radical (Eq. (1)). Firstly, cumene may dissociate its C–H bond photochemically or thermally for molecules with sufficient high thermal energy. Secondly, impurities with available low energy pathway may dissociate into radicals which then react with cumene to form cumyl radicals. Thirdly, the catalyst containing transition metal ion may catalyze the reaction of cumene with oxygen to form cumyl radical and hydrogen peroxide. [16] If CHP is present, it can dissociate into free radicals (Eq. (2)) which in turn react with cumene to form cumyl radicals. In the propagation steps, the cumyl radical reacts with oxygen to form the peroxy radical that abstracts a hydrogen from cumene to regenerate the cumyl radical. In the termination steps, the free radicals in solution combine to form diamagnetic, inactive compounds. Because of the high reactivity of cumyl radical, Eq. (6) and (7) are insignificant in the presence of dioxygen above 13 kPa. [17] In the branching reaction in Eq. (8) [15], the cumyl radical abstracts a hydroxyl group from CHP to form PP. The RO· radical can further react with cumene or cumene hydroperoxide to form the radicals involved in the propagation steps.

In the steady propagation stage of cumene oxidation, the rates of oxygen consumption are constant over a wide range of oxygen pressure $P(O_2)$ until $P(O_2)$ is less than a threshold pressure $P_s$ that increases with the degree of conversion of cumene as shown in Fig. 1 and Fig. 3. This independence of the rate of oxygen consumption, or equivalently the rate of cumene autooxidation, on $P(O_2)$ is easily explained according to the mechanism in Eqs. (1)–(8). The concentration of rad-

icals involved in the propagation steps must be constant because the rapid reactions of radical termination scavenge any excess radicals. The independence on $P(O_2)$ then indicates clearly that hydrogen abstraction in Eq. (4) is the rate determining step in propagation. The increase of $P_s$ on increased cumene conversion is explained by the existence of the branching reaction in Eq. (8). When CHP increases with cumene conversion, the rates of branching reactions also increase. This competing branching reaction leads to an increased $P_s$ with cumene conversion. Since branching reaction leads to formation of PP, one then expects that selectivity to CHP decreases with cumene conversion as observed experimentally. To achieve a high selectivity toward CHP, $P(O_2)$ must always be greater than $P_s$ at the desired cumene conversion. From the curves in Fig. 1 and Fig. 3, at 20% cumene conversion, the $P_s$ values are 59 and 47 kPa for CHP initiated and $Cu(OAc)_2$–CHX-0.6 ( 0.2 g catalyst per 10 ml cumene ) catalyzed cumene autooxidation, respectively.

In the autooxidation of cumene initiated by CHP, the concentration of $ROO^{\cdot}$ must be the maximum allowable concentration in the bulk cumene solution in the steady propagation stage. The concentration of $R^{\cdot}$ must be small in this propagation stage. Therefore, the increased rate of cumene oxidation in the presence of $Cu(OAc)_2$–CHX-0.6 catalyst (0.2 g/10 ml cumene) cannot be due to the increased concentration of $ROO^{\cdot}$ in the bulk solution. However, it is possible that the concentration of $ROO^{\cdot}$ in the vicinity of catalyst exceeds that in the bulk and hence the rate of oxygen consumption is greater. In this case, one would expect that greater amount of catalyst would give greater rate of oxygen consumption. On the contrary, we found that there is an optimal amount of catalyst. Therefore, the concentration of $ROO^{\cdot}$ radical cannot be large near the $Cu(OAc)_2$–CHX-0.6 catalyst. The existence of this optimal amount of $Cu(OAc)_2$–CHX-0.6 catalyst is a clear indication that in the catalyzed cumene autooxidation, there are opposing trends; one favors whereas the other disfavors a large rate of oxygen consumption. As

an increased concentration of ROO˙ is inconsistent with a large rate, it is therefore concluded that the function of $Cu(OAc)_2$–CHX-0.6 is to speed up the rate-determining step in Eq. (4) by increasing the rate constant. The opposing trend is then attributed to a low concentration of ROO˙ in the bulk cause by the presence of the catalyst, $Cu(OAc)_2$–CHX-0.6. When the amount of $Cu(OAc)_2$–CHX-0.6 increases, the concentration of ROO˙ decreases but the rate constants of Eq. (4) increases. The compromise of these two trend leads to an optimal dosage of catalyst. This proposed mechanism also finds support in the behaviors of catalysts and support in the initiation period. The retarding effect of Chelex support is explained by its ability to decrease the concentration of ROO˙. The existence of an optimal amount of $Cu(OAc)_2$–CHX-0.6 in initiating cumene autooxidation can also be perfectly explained according to this mechanism.

$Cu(II)$ ion in $Cu(RCOO)_2$ may have a coordination environment similar to that in $Cu(OAc)_2$–CHX-0.6. $Cu(RCOO)_2$ ($RCOO^-$ = stearate) [18] as a homogeneous catalyst in cumene autooxidation decreases the selectivity to CHP. Therefore, the coordination environment in $Cu(OAc)_2$–CHX-0.6 must differ from that of $Cu(RCOO)_2$ in a homogeneous system.

## 4. Conclusion

We demonstrated that Chelex is a better support than PVP or $SiO_2$ for $Cu(OAc)_2$ as a catalyst in cumene autooxidation to CHP. At 353 K, the autooxidation of cumene catalyzed by $Cu(OAc)_2$–CHX-0.6 used in an amount of 0.2 g for 10 ml cumene has the characteristics of a decreased induction period, a selectivity to CHP better than that initiated with CHP, a rate of cumene autooxidation 63% greater than that initiated by CHP in the steady propagation stage, and a long life time of the $Cu(OAc)_2$–CHX-0.6 catalyst; no deactivation was observed in our experi-

ment. This polymer-supported catalyst is therefore a potentially commercially important catalyst in cumene autooxidation or similar autooxidation processes of hydrocarbons, such as ethylbenzene and isobutane.

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