Polymer supported catalyst for the effective autoxidation of cumene to cumene hydroperoxide

Ying Fang Hsu [a], Cheu Pyeng Cheng [b, *]

[a] *Department of General Education, Fortune Junior College of Technology and Commerce, Chyi Shan, Kaohsiung 842, Taiwan, ROC*
[b] *Department of Chemistry, National Tsing Hua University, Hsin Chu 30043, Taiwan, ROC*

Abstract

The autoxidation of cumene to cumene hydroperoxide (CHP) in the presence of catalyst which was prepared by adsorbing copper(II) acetate onto polymer support, was investigated. When a styrene–divinylbenzene copolymer with sulfonic acid functional groups was used as a support, the resulting catalyst had no catalytic activity. When a macroreticular acrylic polymer containing carboxylic acid exchange groups was used as a support, an effective catalyst was obtained. In the presence of this catalyst (0.2 g $Cu(OAc)_2$-BR-0.6 per 10 mL of cumene) at 353 K, the steady autoxidation rate is 84% faster than that initiated with CHP; the selectivity is 99% at 6.8% conversion. The catalyst is stable at 383 K. Furthermore, the catalyzed cumene autoxidation rate increases linearly with copper acetate loading as well as the amount of catalyst. But when the steady autoxidation rate increases, the selectivity to cumene hydroperoxide reduces, but is still satisfactory. Hence, it is possible to speed up the cumene autoxidation rate by raising the reaction temperature, using catalysts with high metal loading and using more catalyst.

Keywords: Cumene; Autoxidation; Hydroperoxide; Supported catalyst

1. Introduction

The oxidation of hydrocarbons catalyzed by transition metal complexes has been studied extensively [1–4]. Some of these oxidation reactions are important industrial processes in making commodity chemicals such as cyclohexanol, cyclohexanone, ethylbenzene hydroperoxide, *tert*-butyl hydroperoxide, terephthalic acid, adipic acid, cumene hydroperoxide (CHP) and many others [5]. Recently, we discovered that some polymer supported catalysts can catalyze

the reaction between cumene and oxygen [6] to form CHP via a free radical mechanism. An effective catalyst is prepared by supporting $Cu(OAc)_2$ onto Chelex which is a divinylbenzene cross-linked polystyrene with paired iminodiacetate, with a copper(II) content of 0.6 mmol/g of dry support. Using this catalyst at 353 K, the CHP formation rate is 63% higher than that initiated by CHP itself which is a standard industrial process. Furthermore, the selectivity (better than 99% with a conversion ca. 6%) toward CHP of the catalyzed reaction is also better than that initiated by CHP. These results are superior to those catalyzed by free

---

* Corresponding author.

radical initiator [7], by heterogeneous catalysts (Cu, Ag, Pt on support [8]) or by homogeneous catalysts of metal salts (naphthenates of Zn and Cd [9]).

In spite of the above mentioned excellent properties of the $Cu(OAc)_2$ on Chelex supported catalyst, there are some drawbacks. For example, the catalyst undergoes slow decomposition at a reaction temperature of 363 K (vide infra). Therefore, it can not be used at temperature above 363 K. Furthermore, for the catalyzed reaction rate, there is an optimum $Cu(OAc)_2$ loading, as well as an optimum amount of catalyst. Therefore, it is not possible to speed up the reaction rate by employing catalyst with high $Cu(OAc)_2$ loadings or by using more catalyst. We would like to find a supported catalyst which can circumvent these drawbacks and can be of industrial application. Here, we report a polymer supported $Cu(OAc)_2$ catalyst that can be used at 383 K, and possesses the desirable properties of metal loading on catalyst and catalyst loading in the reaction mixture.

2. Experimental

2.1. Material and equipment

Two supports, AG 50W and Bio-Rex 70, both purchased from Bio-Rad, were investigated in this work. AG 50W is a styrene–divinylbenzene copolymer containing sulfonic acid functional groups (5.1 meq/dry g). Bio-Rex 70 is a macroreticular acrylic polymer containing carboxylic acid exchange groups (10 meq/dry g). Cumene (purchased from Merck) was purified by repeated reaction with concentrated sulfuric acid until the acid layer was colorless. It was then washed with water, neutralized with sodium carbonate and washed with water again. After being dried over magnesium sulfate, and refluxed over calcium hydride, cumene was distilled just before use.

The metal contents of the supported catalysts were analyzed on a Kontron Plasmakon model

S-35 ICP instrument. ^1H NMR spectra were recorded on a Germini-300 spectrometer. Cumene and its oxidation products can be identified unambiguously in a ^1H NMR spectrum. In the methyl region, the chemical shifts for the relevant compounds are 1.26 ppm for cumene, 1.61 ppm for CHP, 1.57 ppm for 2-phenyl-2-propanol and 2.61 ppm for acetophenone. From the comparison of the integrated areas of various methyl signals with that of the methyl signal of a methanol internal standard, the concentrations of cumene and its oxidation products can be determined.

2.2. Synthesis of supported catalysts

Bio-Rex 70 (which contained about 65% water as purchased) was dried in a vacuum oven at 323 K until a constant mass was obtained. The dried support was then suspended in water. $Cu(OAc)_2$ of the desired amount was added to the water suspension. After stirring for 1 h, the supported catalyst was collected by filtration. The catalyst was again suspended in methanol under constant stirring for 30 min. After filtration, the catalyst was dried in a vacuum oven at 323 K. In the range of metal loading used in this work, all $Cu(OAc)_2$ used in the preparation was virtually completely adsorbed by the support. The catalyst is designated as $Cu(OAc)_2$-BR-r, where BR indicates that the support is Bio-Rex 70 and r indicates the amount of Cu(II) in mmol per gram of dried support. The values of r in this work are 0.3, 0.6, 1.5, 2 and 2.5. The procedure of preparing $Cu(OAc)_2$ supported on AG 50W was practically the same as that for $Cu(OAc)_2$-BR-r. The AG 50W has a water content of 50% as purchased. The supported catalyst is designated as $Cu(OAc)_2$-AG-r. Only one catalyst with r value 0.6 was prepared for this support.

2.3. Oxidation of cumene

Cumene oxidation was carried out in a closed Pyrex glass system with an oxygen reservoir (0.11 L thermostated at 298 K) and a reaction

flask in which the reaction temperature can be controlled to within ± 1 K. 10 mL of cumene in the reaction flask was used in each reaction run. To monitor the progress of the cumene oxidation reaction, the oxygen pressure was measured by a pressure sensing system which stored all pressure data in a PC. The details of the setup and the experimental procedure were reported previously [6]. The steady cumene autoxidation rate was measured when fresh O_2 was repeatedly admitted to the reaction system when the oxygen pressure dropped below ca. 35 kPa until a steady oxygen consumption rate was obtained. This steady rate was usually reached in the second cycle after the first initiation cycle. The amounts of the cumene oxidation products are determined from ^1H NMR spectra of the oxidation mixture. To be more accurate, an iodometric method [10] was used in the determination of the amount of CHP.

3. Results and discussion

In our previous work on the autoxidation of cumene, $Cu(OAc)_2$-CHX-0.6, where CHX stands for Chelex support and 0.6 indicates the amount of metal loading in unit of mmol of Cu(II) per gram of dry support, was shown to be an effective polymer supported catalyst [6]. Under the autoxidation conditions of 93.3 kPa oxygen pressure, 0.2 g $Cu(OAc)_2$-CHX-0.6 per 10 mL of cumene at 353 K, the steady propagation rate is 1.84×10^{-5} Ms^{-1} which is 63% faster than that of uncatalyzed reaction. And the selectivity is 99.4% at a conversion of 5.36%. However, under identical conditions except at 363 K and repeated introduction of fresh oxygen just before the autoxidation rate slowed down, at a conversion of 33.5%, the color of $Cu(OAc)_2$-CHX-0.6 turned from blue to green. This clearly indicates that $Cu(OAc)_2$-CHX-0.6 is not stable at 363 K. Furthermore, the selectivity to CHP is only 65%. Therefore, in the presence of $Cu(OAc)_2$-CHX-0.6, it is not possible to speed up the cumene oxidation rate by

raising the temperature. Also, it is not possible to increase the rate by using more catalyst or using catalyst with higher metal loading as mentioned in the introduction. Hence, one is left with the only choice of resorting to other catalyst, if one wants to have a high reaction rate. In our previous work [6], we demonstrated that the inorganic support, SiO_2, though stable, can lead to conversion of CHP to 2-phenyl-2-propanol which is consistent with the literature report [11]. We have also shown that when polyvinylpyridine is used to support $Cu(OAc)_2$, the selectivity to CHP is poor and the polymer itself is oxidized. Therefore, from our success with Chelex, we thought that polymer supports with acidic functional groups are more likely to be effective.

3.1. Effect of support

In our study [6] of the cumene autoxidation rate catalyzed by MS-CHX-0.6 as a function of metal salt (MS), we found the effectiveness of the metal ion follows the order:
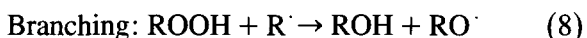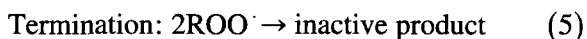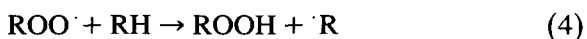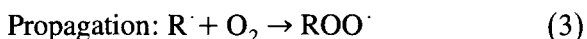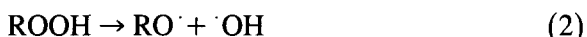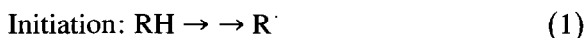
$$Mn(II) > Cu(II) > Co(II) > Ni(II) > Fe(II)$$
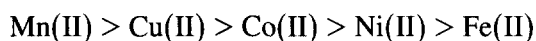
The CHP selectivity of the Mn(II) catalyst is less than that of Cu(II). Furthermore, we also found that among the various copper(II) salts, including acetate, sulfate, nitrate, chloride and bromide, the acetate is superior to the other anions in terms of reaction rate [1]. Therefore, we chose to study $Cu(OAc)_2$ adsorbed on AG 50W and Bio-Rex 70 (abbreviated as AG and BR, respectively) as our catalysts.

In Fig. 1, the oxygen pressures are shown as a function of time in the cumene autoxidation

---

[1] Catalysts of various copper (II) salts adsorbed onto Chelex 100 with the same number of moles (0.6) per gram of support were investigated under identical reaction conditions: 0.2 g supported catalyst in 10 mL of cumene, initial O_2 pressure 93.3 kPa at 353 K. The steady autoxidation rates are 1.91×10^{-5}, 0.56×10^{-5}, 0.54×10^{-5}, 0.46×10^{-5} and 0.42×10^{-5} M/s in the presence of catalyst of supported copper (II) acetate, copper (II) sulfate, copper (II) nitrate, copper (II) chloride and copper (II) bromide, respectively.

which is carried out in a closed system containing 10 mL of cumene, at 353 K, 0.2 g of catalyst and initial oxygen pressure of 93.3 kPa. $Cu(OAc)_2$-AG-0.6 does not catalyze the cumene autoxidation reaction at all. On the contrary, it inhibits the autoxidation reaction. However, $Cu(OAc)_2$-BR-0.6 is an effective catalyst for the cumene autoxidation reaction. After an induction period of about 3 h, the oxygen pressure drops continuously until a pressure of 26.7 kPa is reached, then the pressure drop slows down. When oxygen is added to the closed reaction system again, rapid oxygen consumption is established immediately. The variation of the oxygen consumption rate can be explained by the mechanism of the autoxidation of cumene [12–14], as shown below.

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

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

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

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

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

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

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

$$\text{Branching: } ROOH + R^{\cdot} \rightarrow ROH + RO^{\cdot} \qquad (8)$$

The existence of the initial induction period is a general phenomenon in initiating a free radical reaction by Eqs. (1) and (2). The nearly constant oxygen consumption rate after the initiation period is an indication that the rate determining step in the free radical reaction is independent of the O_2 pressure. The hydrogen abstraction reaction in Eq. (4) is then the rate determining step. The slowing down of oxygen consumption at a pressure below 26.7 kPa is due to the branching reaction Eq. (8) [14]. This association of branching reaction with slow oxygen consumption is further supported by the observation that if the autoxidation reaction stays in the slow down region longer, then the selectivity to CHP is reduced and selectivity to 2-phenyl-2-propanol is increased. Therefore, it is
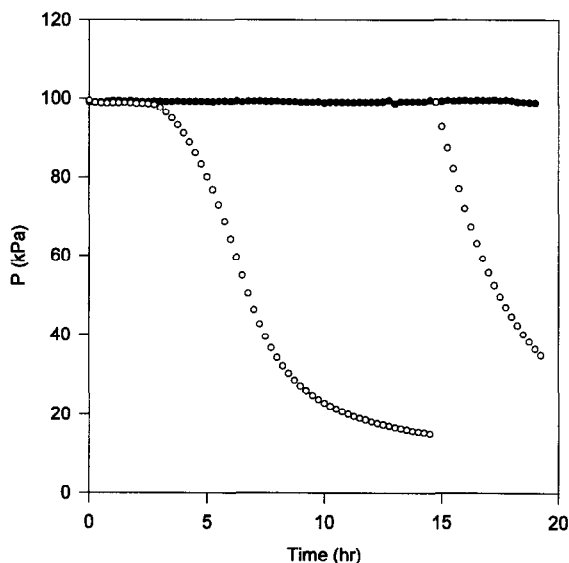

Fig. 1. At 353 K, the pressure of oxygen $P(O_2)$ ($V = 0.11$ L) as a function of reaction time in the autoxidation of cumene (10 mL) in the presence of catalyst (0.2 g); (●): $Cu(OAc)_2$-AG-0.6, (○): $Cu(OAc)_2$-BR-0.6.

necessary to maintain a sufficient high oxygen pressure such that the branching reaction is slow in comparison with the propagation reaction Eqs. (3) and (4) if a high selectivity to CHP is desirable.

3.2. Effect of temperature

The catalytic activity of $Cu(OAc)_2$-BR-0.6 was investigated as a function of temperature. The oxygen pressure variation in a reaction mixture of 10 mL of cumene with 0.2 g $Cu(OAc)_2$-BR-0.6 at initial oxygen 93.3 kPa as a function of time at 353, 363, 373 and 383 K are shown in Fig. 2. After O_2 pressure around 40 ~ 50 kPa was reached in the initial reaction period, fresh O_2 was introduced to commence a second reaction period. It is clear that the higher the reaction temperature, the shorter the induction period; it shortens from 4 h at 353 K to ca. 30 min at 383 K. The steady oxygen consumption rate (calculated from oxygen pressure drop in the second period) also speeds up with temperature increase. The ^{1}H NMR spectrum of the product mixture of cumene oxidation shows that
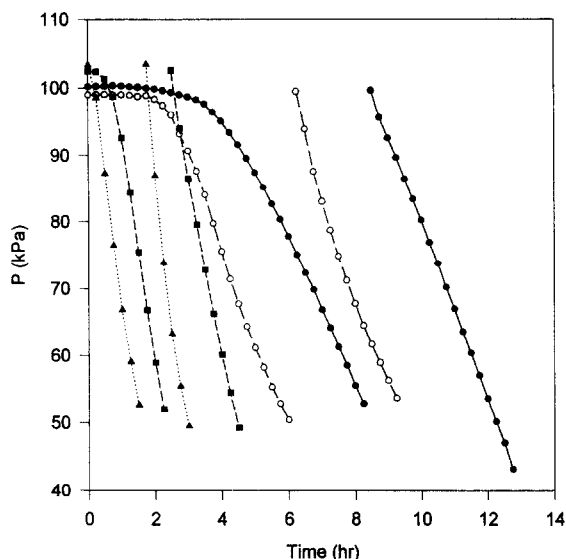
Fig. 2. The pressure of oxygen $P(O_2)$ ($V = 0.11$ L) as a function of reaction time in the autoxidation of cumene (10 mL) in the presence of $Cu(OAc)_2$-BR-0.6 (0.2 g) at various temperature: (●): 353 K, (○): 363 K, (■): 373 K, (▲): 383 K.

besides cumene and CHP, 2-phenyl-2-propanol is the only side product. The steady reaction rate, conversion and selectivity at the end of the second period are collected in Table 1. At 353 K, the rate of cumene autoxidation in the presence of 0.2 g of $Cu(OAc)_2$-BR-0.6 is 13% faster than that in the presence of 0.2 g of $Cu(OAc)_2$-CHX-0.6. This rate is 84% higher than that initiated by CHP. At 383 K, the rate is 3.7 times that at 353 K. The apparent activation energy is

37.6 kJ mol^{-1}. More importantly, there is no sign of decay of the $Cu(OAc)_2$-BR-0.6 catalyst at 383 K. Therefore, the instability in the Chelex supported catalyst can be overcome by using Bio-Rex support. The Bio-Rex supported catalyst also has a high selectivity, at 383 K, a satisfactory selectivity of 94.4% was found.

3.3. Effect of copper acetate loading

At 363 K, the results of the autoxidation of cumene in the presence of constant amount of $Cu(OAc)_2$-BR-r, where r ranges from 0.3 to 2.5, are collected in Table 2. When the metal loading increases, the steady autoxidation rate increases. It is noteworthy that the rate increases linearly by a factor of 1.78 when r changes from 0.3 to 2.5. This linear variation of autoxidation rate as a function of r is distinctly different from that of the $Cu(OAc)_2$-CHX-r catalyzed reaction where an optimum rate is observed at $r = 0.6$.

But the catalyst with high metal loading has the detrimental effect of reducing the selectivity to CHP. More precisely, the selectivity to the undesirable 2-phenyl-2-propanol increases faster than linearly by a factor of 3.1 when r changes from 0.3 to 2.5. Therefore, a balance in rate and selectivity must be considered in an application. The effectiveness of the copper ions can be judged by the ratio of autoxidation rate per

Table 1

Product distribution and rate of the autoxidation of cumene (10 ml) in the steady propagation stage in the presence of $Cu(OAc)_2$-BR-0.6 (0.2 g) at various temperatures; initial $P(O_2)$: 93.3 kPa ($V = 0.11$ L)

Temperature (K)	α [a] (%)	$\Delta n(O_2)$ [b] (mmol)	CHP [c] (mmol)	PP [d] (mmol)	S(CHP) [e] (%)	Rate [f] (10^{-5} M/s)
353	6.80	4.85	4.81	0.05	99.0	2.06
363	6.39	4.54	4.46	0.11	97.6	2.76
373	7.17	5.09	4.90	0.23	95.6	4.05
383	7.20	5.06	4.86	0.29	94.4	7.42

[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] S(CHP) denotes selectivity to CHP relative to cumene reacted.
[f] Rate is the steady oxygen consumption rate.

Table 2
Product distribution and rate of autoxidation of cumene (10 ml) in the steady propagation stage in the presence of catalyst (0.2 g) at 363 K; initial P(O$_2$): 93.3 kPa ($V = 0.11$ L) as a function of metal loading in Cu(OAc)$_2$-BR-r.

Catalyst	α (%)	Δn(O$_2$) (mmol)	CHP (mmol)	PP (mmol)	S(CHP) (%)	Rate (10^{-5} M/s)	R [a] (10^{-4} M/s)
Cu(OAc)$_2$-BR-0.3	7.08	5.05	4.96	0.10	98.0	2.67	4.45
Cu(OAc)$_2$-BR-0.6	6.39	4.54	4.46	0.11	97.6	2.76	2.30
Cu(OAc)$_2$-BR-1.5	7.69	5.51	5.30	0.20	96.3	4.05	1.35
Cu(OAc)$_2$-BR-2.0	6.09	4.27	4.15	0.21	95.2	4.38	1.10
Cu(OAc)$_2$-BR-2.5	7.08	5.01	4.75	0.31	93.8	4.74	0.95

All notations are the same as specified in Table 1.
[a] R is the rate per mmol of Cu(OAc)$_2$ supported on each gram of dry support; it is given by rate/r.

mmol of Cu(OAc)$_2$ in the support. The data in the last column of Table 2, clearly indicate that the effectiveness of the copper ions decreases monotonically with increasing loading.

3.4. Effect of the amount of catalyst

At 363 K, the results of autoxidation of cumene in the presence of various amount of Cu(OAc)$_2$-BR-0.6 are collected in Table 3. When the amount of catalyst increases from 0.05 to 0.5 g per 10 mL of cumene, the steady rate of autoxidation increases linearly from 1.42 $\times 10^{-5}$ to 4.41 $\times 10^{-5}$ M s^{-1}. Therefore, one could use large amount of Cu(OAc)$_2$-BR-0.6 catalyst to increase the autoxidation rate. This dependence on the amount of Cu(OAc)$_2$-BR-0.6 is different from that in the Cu(OAc)$_2$-CHX-0.6 catalyzed reaction in which there is an optimum amount of Cu(OAc)$_2$-CHX-0.6 for the steady autoxidation rate [6]. However, when the amount

of catalyst increases by a factor of 10, the autoxidation rate increases only by a factor of 3.10. The effectiveness of the Cu(OAc)$_2$-BR-0.6 catalyst per gram, measured by the autoxidation rate divided by the mass of catalyst, is shown in the last column of Table 3. It is obvious that the effectiveness decreases with increasing amount of catalyst. There is also a drawback in selectivity when a large amount of catalyst is used. The selectivity to 2-phenyl-2-propanol increases faster than linearly with the increase of the amount of catalyst. There is an increase of 6.3 fold in selectivity to 2-phenyl-2-propanol for an increase of 10 fold in the amount of catalyst.

3.5. The enhancement of cumene autoxidation rate

The reaction mechanism of the Cu(OAc)$_2$-BR-r catalyzed reaction should be the same as that catalyzed by Cu(OAc)$_2$-CHX-0.6 [6]; it is

Table 3
Product distribution and rate of autoxidation of cumene (10 ml) in the steady propagation stage in the presence of various amounts of Cu(OAc)$_2$-BR-0.6 at 363 K; initial P(O$_2$): 93.3 kPa ($V = 0.11$ L)

Amount of catalyst (g)	α (%)	Δn(O$_2$) (mmol)	CHP (mmol)	PP (mmol)	S(CHP) (%)	Rate (10^{-5} M/s)	R [a] (10^{-4} M/s)
0.05	7.43	5.32	5.25	0.06	98.9	1.42	2.84
0.1	5.64	4.03	3.98	0.05	98.8	1.70	1.70
0.2	6.39	4.54	4.46	0.11	97.6	2.76	1.38
0.3	5.30	3.75	3.68	0.11	97.1	2.99	0.99
0.4	5.24	3.68	3.54	0.21	94.4	3.63	0.91
0.5	6.89	4.81	4.58	0.35	93.0	4.41	0.88

All notations are the same as specified in Table 1.
[a] R is the rate per gram of Cu(OAc)$_2$-BR-0.6 catalyst in cumene (10 mL); it is given by rate/amount of catalyst.

basically a free radical reaction mechanism as indicated in Eqs. (1)–(8). The rate determining step is the hydrogen abstraction from cumene by cumyl hydroperoxy radical (Eq. (4)). Since the catalyzed reaction is heterogeneous, reactions in the bulk solution and near the catalyst surface must occur simultaneously. The former reaction is not different from the CHP-initiated reaction. The latter reaction must then contribute to the enhanced rate. The catalyst can increase the steady-state concentration of ROO· radical. Alternatively, the catalyst may also reduce the activation energy in Eq. (4). Our experimental data seems to be consistent with the increase of the steady-state level of ROO· (vide infra). We showed that when metal loading increases, the autoxidation rate also increases, but the effectiveness of the Cu(II) centers decreases. This may be due to that some of the Cu centers are imbedded inside the polymer that reactants and products can not easily diffuse to and from those Cu centers. We have also shown that the reaction rate also increases with the amount of catalyst. Again the effectiveness of the individual copper center decreases. The decrease in the effectiveness can not be explained by the same argument used in the explanation of the metal loading effect. This may be caused by the impeding effect of the support which is the proposed mechanism in explaining the existence of an optimum amount of Cu(OAc)₂-CHX-0.6 catalyst [6]. At 363 K, we measured the steady autoxidation rates of cumene in the presence of 0.2 g of Cu(OAc)₂-BR-0.6 in 10 mL of cumene with or without additional dry support Bio-Rex 70. The rates are 2.76×10^{-5}, 2.78×10^{-5}, and 2.69×10^{-5} M s^{-1} in the presence of 0, 0.050 and 0.100 g Bio-Rex 70 respectively. These data clearly indicate that Bio-Rex 70 does not impede the autoxidation of cumene. This is in contrast with the Chelex support. Therefore, the reduced effectiveness of metal centers at large amount of catalyst is not due to support. However, this reduced effectiveness can be explained qualitatively by assuming that the major effect of the catalyst is to increase the steady-

state level of ROO·. When more catalyst is used, then ROO· concentration should be increased. This increase is counteracted to some extent by the increased termination rate in Eqs. (5) and (7). Therefore, the effectiveness of individual centers is decreased with increased catalyst loading. Moreover, this catalytic mechanism can also explain at least partially the reduced effectiveness of the individual copper center with increased Cu(II) loading. The selectivity to CHP decreases by using catalyst with high metal loading or using large amount of catalyst. Examining the selectivity to 2-phenyl-2-propanol, it seems that the selectivity has a quadratic dependence on either the metal loading or on the amount of catalyst. These dependencies seem to indicate that the formation of 2-phenyl-2-propanol by a two-copper-center process may be important.

4. Conclusion

We show that for cumene autoxidation, Cu(OAc)₂-BR-*r* is a very effective catalyst. As a support Bio-Rex 70 is superior than AG 50W, SiO₂, Chelex and polyvinylpyridine. Unlike Chelex, Bio-Rex 70 does not hinder the autoxidation of cumene regardless whether the catalyst is present or not. This Cu(OAc)₂-BR-*r* catalyst possesses the following desirable properties: (a) it is stable at 383 K; (b) the catalyzed reaction rate increases linearly with copper acetate loading; and (c) the catalyzed reaction rate also increases linearly with the amount of catalyst. However, the selectivity decreases when the catalyzed reaction is carried out at high temperature, in the presence of catalyst with high metal loading, or in the presence of a large amount of catalyst. Therefore, in actual application, a balance between rate and selectivity must be optimized. But our finding that the Cu(OAc)₂-BR-*r* catalyst has a high temperature stability is important in that it may be used with other substrates such as ethylbenzene and isobutane which require high temperature for effec-

tive peroxidation reaction. Work along this direction are in progress.

Acknowledgements

References

[1] M. Fetizon, W.J. Thomas (Eds.), The Role of Oxygen in Improving Chemical Processes (The Royal Society of Chemistry, Cambridge, 1993).

[2] G.W. Parshall and S.D. Ittel, Homogeneous Catalysis, 2nd Ed. (Wiley, New York, 1992).

[3] D.T. Sawyer, Oxygen Chemistry (Oxford University Press, Oxford, 1991).

[4] D.H.R. Barton, A.E. Martell and D.T. Sawyer (Eds.), The Activation of Dioxygen and Homogeneous Catalytic Oxidation (Plenum Press, New York, 1993).

[5] K. Weissermel and H.-J. Arpe, Industrial Organic Chemistry, translated by C.R. Lindley, 2nd Ed. (VCH, New York, 1993).

[6] Y.F. Hsu, M.H. Yen and C.P. Cheng, J. Mol. Catal. 105 (1996) 137.

[7] K. Hattori, H. Kubota, H. Suzuki, T. Ikawa and Y. Tanaka, J. Chem. Eng. Jpn. 13 (1970) 72.

[8] N.H.A. Van Han, B.E. Nieuwenhuys and W.M.H. Sachtler, J. Catal. 20 (1971) 408.

[9] S.K. Kozlov, F.I. Tovstokhatko and V.M. Potekhin, J. Appl. Chem. USSR. 58 (1985) 2490.

[10] C.D. Wanger, R.H. Smith and E.D. Peters, Anal. Chem. 19 (1947) 976.

[11] J.H.R. Casemier, B.E. Nieuwenhuys and W.M.H. Sachtler, J. Catal. 29 (1973) 367.

[12] C. Walling, Free Radicals in Solution, Vol. II (Wiley, New York, 1957).

[13] J.K. Kochi (Ed.), Free Radicals, Vol. II (Wiley, New York, 1973).

[14] J.K. Kochi (Ed.), Free Radicals, Vol. I (Wiley, New York, 1973).