

Mechanistic investigation of the autooxidation of cumene catalyzed by transition metal salts supported on polymer

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Abstract

The autooxidations of cumene to cumene hydroperoxide (CHP) in the presence of various transition metal salts supported on Bio-Rex 70 which is a macroreticular polyacrylate with carboxylate functional group, were investigated. The polymer supported catalyst is denoted as MS-BR-*r* in which MS represents transition metal salt, BR represents the polymer support and *r* is the loading of metal salt in the unit of mmoles per gram of dry support. In a catalyst loading of 0.20 g per 10 ml of cumene and initial O₂ pressure 103 kPa at 363 K, the catalyzed autooxidation rate follows the order: Mn(OAc)₂-BR-0.6 > Co(OAc)₂-BR-0.6 > FeCl₂-BR-0.6 > Cu(OAc)₂-BR-0.6 > Cr(NO₃)₃-BR-0.6 ≫ Ni(OAc)₂-BR-0.6. The selectivities to CHP are 97% for Cu(OAc)₂-BR-0.6 and Cr(NO₃)₃-BR-0.6; and 92% for Mn(OAc)₂-BR-0.6, Co(OAc)₂-BR-0.6 and FeCl₂-BR-0.6. These data indicate that Cu(OAc)₂-BR-0.6 is the best catalysts among the catalysts investigated in this work. The metal loading effect was investigated for Co(OAc)₂-BR-*r*, *r* = 0.3, 0.6, 1.5, 2.0 and 2.5. In the catalyst loading of 0.20 g per 10 ml of cumene and initial O₂ pressure 100 kPa at 363 K, the oxidation rate increases with *r* from 3.96 × 10⁻⁵ M/s at *r* = 0.3 to 8.35 × 10⁻⁵ M/s for *r* = 2.5. The selectivity to CHP decreases with increasing *r* from 93.8% for *r* = 0.3 to 88.1% for *r* = 2.5 at a conversion of 7%. When cumene autooxidation catalyzed by Co(OAc)₂-BR-2.0 was investigated at temperatures in the range of 363 K to 323 K, we found that oxidation rate decreases with temperature. However, unexpectedly, the selectivity decreases with temperature. This is interpreted by considering the competing reactions between the formation of CHP which has a high activation energy and the catalyzed redox decomposition of CHP which has a low activation energy. When temperature decreases, the rate of formation of CHP decreases more than that of the decomposition of CHP. When the autooxidation is catalyzed by a small amount of soluble copper(II) laurate or copper(II) stearate, the oxidation rate is faster and the selectivity to CHP is lower than that catalyzed by Cu(OAc)₂-BR-0.6 under similar reaction conditions. The carboxylate coordination environment on copper(II) reaction center is not sufficient for Cu(OAc)₂-BR-0.6 to be an effective catalyst in cumene autooxidation. We propose that the role played by the polymer support is that the backbone of the polymer reduces the rate of the catalyzed redox decomposition of CHP by hindering the change of the coordination environments on the copper center during the redox decomposition reaction of CHP. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cumene; Polymer; Transition metal salt

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1. Introduction

Autooxidations of organic compounds are important industrial processes in producing commodity chemicals [1–10]. Reaction of cumene with oxygen to produce cumene hydroperoxide (CHP) is one of such autooxidations. In the Hercules and in the Allied industrial processes, the operating temperatures are 353–393 K; the pressures are 100–600 kPa (air); reaction times are 4–20 h; selectivities to CHP are in the range of 90–96%; initiator is CHP. The major difference between the two commercial processes is that acid neutralizing Na_2CO_3 is added to the reaction medium in the Hercules process, whereas in the Allied process, the reaction medium is washed with aqueous NaOH solution to keep the reaction medium in basic condition. The autooxidation in the presence of metal salts, either homogeneously or heterogeneously [11,12], has been investigated to find the possible improvement in the operating conditions on the selectivity. Unfortunately, all metal salt catalysts that have been investigated so far, lead to a decreased selectivity to CHP despite an accelerated autooxidation rate. One possible approach to increase the selectivity of CHP in the catalyzed reaction is to carry out the catalytic reaction at a reduced temperature. One of the main object of this work is to look into the effect of temperature reduction in the transition metal salt catalyzed autooxidation of cumene.

Recently, we reported [13,14] that the catalysts which were prepared by supporting copper(II) acetate on polymers, can be very effective in catalyzing the autooxidation of cumene. The nature of support has a great influence on the performance of the supported catalyst. For example, polyvinylpyridine is oxidized under the cumene autooxidation condition. The catalyst with $\text{Cu}(\text{OAc})_2$ supported on AG 50 W polymer (trade name of Bio-Rad, a styrene-divinylbenzene polymer containing sulfonate functional group) does not have any catalytic activity. However, we found that two polymer

supports, Chelex-100 (a trade name of Bio-Rad, a styrene-divinylbenzene copolymer containing imino-diacetate functional group) and Bio-Rex 70 (trade name of Bio-Rad, a macroreticular acrylate polymer containing carboxylate functional group), yield catalysts that are effective in terms of a higher reaction rate and a better selectivity to CHP in cumene autooxidation than those initiated by CHP. The Bio-Rex supported copper acetate catalyst is particularly attractive for industrial application in that the catalyst can increase the reaction rate by a factor of two compared to that initiated with CHP, and the selectivity to CHP is also better.

In this article, we investigate the effectiveness of the catalyst prepared by supporting various transition metal salts on Bio-Rex 70. Some of the transition metal salts supported catalysts give a high autooxidation rate. With this enhanced reaction rate, it is possible to study the autooxidation reaction rate at a reduced temperature. We found that the selectivity to CHP deteriorates when the reaction temperature for the catalyzed autooxidation of cumene decreases in contrast to the common accepted notion that a lower reaction temperature should lead to a better selectivity. In addition, the effectiveness of $\text{Cu}(\text{OAc})_2$ supported on Bio-Rex 70 and soluble copper(II) carboxylate in the catalyzed cumene autooxidation, were compared in this work to understand the role played by the polymer support.

2. Experimental

2.1. Material and equipment

Bio-Rex 70 (purchased from Bio-Rad) 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.

Copper(II) laurate, CuLu_2 , and Copper(II) stearate, CuSt_2 , were prepared by the direct reactions of copper(II) acetate with lauric acid and stearic acid (both acids were purchased from Showa Chemical (Tokyo), in a 1:2 molar ratio in methanol. The solution in which lauric acid or stearic acid is suspended, was stirred for 12 h. The blue color in the solution faded completely and the suspension became blue. After filtering the resulting Cu(II) carboxylate was washed repeatedly with methanol and dried in a vacuum oven at 323 K. The elemental analyses results are given below. For CuLu_2 , found (theoretical, $\text{C}_{24}\text{H}_{46}\text{O}_2\text{Cu}$) %: C: 68.3(68.6), H: 10.7(11.1), Cu: 10.4(10.2). For CuSt_2 , found (theoretical, $\text{C}_{36}\text{H}_{70}\text{O}_2\text{Cu}$) %: C: 63.1(62.3), H: 9.87(9.96), Cu: 13.3(13.9).

The metal contents of the catalysts were analyzed on a Kontron Plasmakon model S-35 ICP instrument. Elemental Analysis of results were obtained on a Perkin–Elmer 240C-2400 EA instrument. ^1H NMR spectra were recorded on a Gemini-300 or Unity-400 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 in CDCl_3 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 and the metal salt to be impregnated was then added. 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 loadings used in this work, all metal salt used in the preparation was virtually completely adsorbed by the support. The catalyst is designated as MS-BR- r , in which MS represents the transition metal salt; BR indicates that the support is Bio-Rex 70 and r indicates the amount of MS in mmol per gram of dried support. The catalyst prepared include $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$, $\text{Co}(\text{OAc})_2\text{-BR-}r$ ($r = 0.3, 0.6, 1.5, 2.0$ and 2.5), $\text{Mn}(\text{OAc})_2\text{-BR-0.6}$, $\text{Ni}(\text{OAc})_2\text{-BR-0.6}$, $\text{FeCl}_2\text{-BR-0.6}$, $\text{Cr}(\text{NO}_3)_3\text{-BR-0.6}$.

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. A 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 [13]. The cumene auto-oxidation rate was measured when fresh O_2 was repeatedly admitted to the reaction system after the oxygen pressure dropped below ca. 47 kPa until a steady oxygen consumption rate was obtained. This steady rate was usually reached in the second cycle after the first initiation cycle. When the oxidation rate in the second cycle varies with oxygen pressure, we take the rate measured in the initial part of the second cycle as the rate of autooxidation. The amounts of the cumene oxidation products are determined from ^1H NMR spectra of the oxidation mixture. To be more accurate, an iodometric method [15] was used in determining the amount of CHP.

3. Results and discussion

3.1. Autooxidation of cumene catalyzed by the transition metal salts supported on polymer

We prepared a series of catalysts in which various transition metal salts, including $\text{Ni}(\text{OAc})_2$, $\text{Cr}(\text{NO}_3)_3$, $\text{Co}(\text{OAc})_2$, $\text{Mn}(\text{OAc})_2$, FeCl_2 and $\text{Cu}(\text{OAc})_2$, were supported on Bio-Rex 70 which is a macroreticular polyacrylate with carboxylate functional group. These catalysts are denoted as MS-BR- r , in which MS represents the transition metal salt, BR is an abbreviation for Bio-Rex 70 polymer support and r is the number of mmoles of metal salt per gram of dried polymer support. The effectiveness of these catalysts in catalyzing the autooxidation of cumene was investigated at 363 K. The results in Fig. 1 indicate that in the presence of $\text{Ni}(\text{OAc})_2$ -BR-0.6, no autooxidation of cumene can be detected after a reaction period of 10 h at 363 K. The reaction with $\text{Cr}(\text{NO}_3)_3$ -BR-0.6 has a long induction period of 5.5 h.

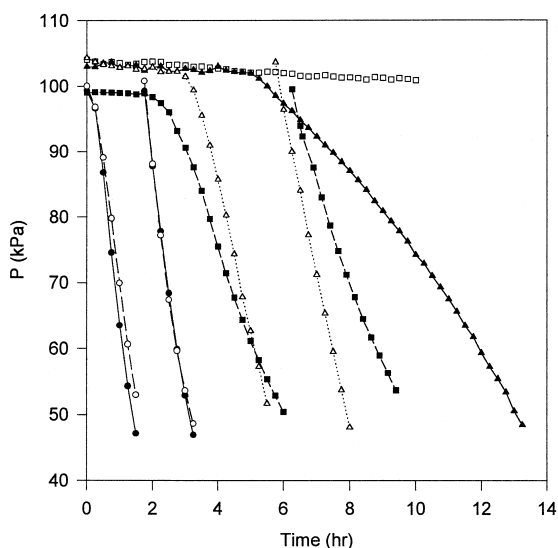


Fig. 1. At 363 K, the pressure of oxygen $P(\text{O}_2)$ ($V = 0.11$ l) as a function of reaction time in the autooxidation of cumene (10 ml) in the presence of catalyst (0.20 g): (●): $\text{Mn}(\text{OAc})_2$ -BR-0.6, (○): $\text{Co}(\text{OAc})_2$ -BR-0.6, (■): $\text{Cu}(\text{OAc})_2$ -BR-0.6 (data from Ref. [14]), (△): FeCl_2 -BR-0.6, (▲): $\text{Cr}(\text{NO}_3)_3$ -BR-0.6, (□): $\text{Ni}(\text{OAc})_2$ -BR-0.6.

The induction period follows the order: $\text{Co}(\text{OAc})_2$ -BR-0.6 \approx $\text{Mn}(\text{OAc})_2$ -BR-0.6 < $\text{Cu}(\text{OAc})_2$ -BR-0.6 < FeCl_2 -BR-0.6 < $\text{Cr}(\text{NO}_3)_3$ -BR-0.6 < $\text{Ni}(\text{OAc})_2$ -BR-0.6.

After the induction period, the oxygen pressure dropped rapidly. When the oxygen pressure dropped below 47 kPa, fresh oxygen was introduced into the closed reaction system, rapid oxygen pressure drop was observed except the case of $\text{Ni}(\text{OAc})_2$ -BR-0.6 and $\text{Cr}(\text{NO}_3)_3$ -BR-0.6 catalysts. If fresh oxygen was added to the reaction system, after the second cycle, rapid oxygen consumption as in the second cycle was detected. The rate of oxygen consumption in the third cycle is almost identical to that in the second cycle. Therefore, the oxygen consumption rate in the second cycle can be used as an indication of oxygen consumption rate. In the case that the oxygen consumption in the second cycle is slightly dependent on the oxygen pressure, we take the average of the consumption rate in the initial period of the second cycle as a measure of the autooxidation rate. The oxygen consumption rate is inversely correlated with the induction period, except for FeCl_2 -BR-0.6 and $\text{Cu}(\text{OAc})_2$ -BR-0.6 catalysts. In these two catalytic reactions, the rate for $\text{Cu}(\text{OAc})_2$ -BR-0.6 is less than that of FeCl_2 -BR-0.6, in agreement with their relative magnitudes of induction periods.

^1H NMR spectra of the catalyzed reaction mixtures indicate that CHP and 2-phenyl-2-propanol (PP) are the only oxidation products. The amounts of products and the selectivity to CHP for the cumene autooxidation in the presence of a variety of polymer supported catalysts are shown in Table 1. When the conversion of cumene is controlled in the range of 7%, which corresponds to an oxygen pressure drop ca. 110 kPa in our experimental setup, the selectivities for the FeCl_2 -BR-0.6, $\text{Co}(\text{OAc})_2$ -BR-0.6 and $\text{Mn}(\text{OAc})_2$ -BR-0.6 catalysts are about 92%. This selectivity is comparable with that of CHP initiated reaction. For $\text{Cr}(\text{NO}_3)_3$ -BR-0.6 and $\text{Cu}(\text{OAc})_2$ -BR-0.6 catalysts, the selectivities are about 97%. Since the reaction rate of $\text{Cr}(\text{NO}_3)_3$ -

Table 1

Product distribution and rate of the autooxidation of cumene (10 ml) in the presence of various catalyst (0.20 g) at 363 K; initial $P(O_2)$: 103 kPa ($V = 0.11$ l)

Catalyst	α^a (%)	$\Delta n(O_2)^b$ (mmol)	CHP ^c (mmol)	PP ^d (mmol)	S(CHP) ^e (%)	Rate ^f (10^{-5} M/s)
CHP ^g	5.94	4.18	3.91	0.34	92.1	2.28
Ni(OAc) ₂ -BR-0.6	—	—	—	—	—	—
Cr(NO ₃) ₃ -BR-0.6	8.01	5.66	5.56	0.17	97.0	2.23
Cu(OAc) ₂ -BR-0.6 ^h	6.39	4.54	4.46	0.11	97.6	2.76
FeCl ₂ -BR-0.6	7.39	5.10	4.82	0.47	91.2	3.81
Co(OAc) ₂ -BR-0.6	6.62	4.56	4.41	0.32	93.2	5.40
Mn(OAc) ₂ -BR-0.6	7.38	5.19	4.90	0.38	92.8	6.21

^aConversion of cumene.

^bAmount of oxygen reacted.

^cCHP denotes cumene hydroperoxide, determined by iodometric method.

^dPP denotes 2-phenyl-2-propanol, analyzed by ¹H NMR spectroscopy.

^eS(CHP) denotes selectivity to CHP relative to cumene reacted.

^fRate is the oxygen consumption rate.

^gThe amount of CHP added is 0.64 g.

^hData from Ref. [14].

BR-0.6 catalyzed reaction is slow, Cu(OAc)₂ supported on Bio-Rex polymer is the best catalyst among those in Table 1. This conclusion is similar to what we have found when Chelex was used as support [13]. Though Co(OAc)₂-BR-0.6 has the drawback of low selectivity, we like to look more carefully into the effect of Co(OAc)₂ loading and temperature to find the factors influencing the selectivity in the hope of gaining more understanding on the characteristics of the polymer supported catalyst.

3.2. Effect of Co(OAc)₂ loading on the catalytic autooxidation of cumene

The oxygen consumption curves for the cumene autooxidation reactions in the presence of Co(OAc)₂-BR- r ($r = 0.3, 0.6, 1.5, 2.0$ and 2.5) are shown in Fig. 2. The induction period decreases from 2.5 h for $r = 0.3$ to 0.3 h for $r = 0.6$. For $r \geq 1.5$, there is no noticeable induction period. The oxygen consumption rate increases with r . When the conversion is limited to ca. 7%, the results of the reaction product analyses are collected in Table 2. It is obvious that when metal loading increases, the selectivity decreases steadily from 93.8% for $r = 0.3$ to 88.1% for $r = 2.5$. The oxidation

rates increases with r from 3.95×10^{-5} M/s for $r = 0.3$ to 8.35×10^{-5} M/s for $r = 2.5$. The trade-off between selectivity and reaction rate as a function of r is obvious; a slower reaction rate gives a better selectivity.

The normalized oxidation rates, defined as the oxidation rate per unit metal loading per

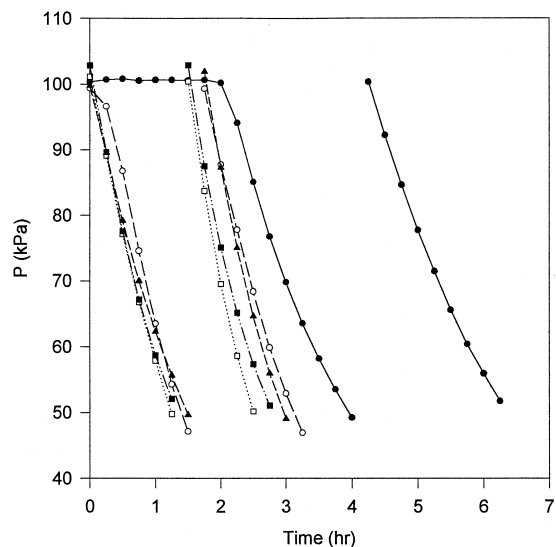


Fig. 2. At 363 K, the pressure of oxygen $P(O_2)$ ($V = 0.11$ l) as a function of reaction time in the autooxidation of cumene (10 ml) in the presence of catalyst (0.20 g); (●): Co(OAc)₂-BR-0.3, (○): Co(OAc)₂-BR-0.6, (▲): Co(OAc)₂-BR-1.5, (■): Co(OAc)₂-BR-2.0, (□): Co(OAc)₂-BR-2.5.

Table 2

Product distribution and rate of autooxidation of cumene (10 ml) in the presence of catalyst (0.20 g) at 363 K; initial $P(\text{O}_2)$: 100 kPa ($V = 0.11$ l) as a function of metal loading in $\text{Co}(\text{OAc})_2\text{-BR-}r$

Catalyst	α (%)	$\Delta n(\text{O}_2)$ (mmol)	CHP (mmol)	PP (mmol)	S(CHP) (%)	Rate (10^{-5} M/s)	R^a (10^{-4} M/s)
$\text{Co}(\text{OAc})_2\text{-BR-0.3}$	6.84	4.75	4.58	0.31	93.8	3.96	6.60
$\text{Co}(\text{OAc})_2\text{-BR-0.6}$	6.62	4.56	4.41	0.32	93.2	5.40	4.50
$\text{Co}(\text{OAc})_2\text{-BR-1.5}$	7.34	5.00	4.60	0.65	87.7	7.71	2.57
$\text{Co}(\text{OAc})_2\text{-BR-2.0}$	6.95	4.68	4.36	0.61	87.7	8.15	2.04
$\text{Co}(\text{OAc})_2\text{-BR-2.5}$	7.49	5.05	4.72	0.64	88.1	8.35	1.67

All notations are the same as specified in Table 1.

^a R is the rate per mmol of $\text{Cu}(\text{OAc})_2$ supported on each gram of dry support; it is given by rate divided by metal loading r and the amount of catalyst.

gram of supported catalyst, are listed in the last column of Table 2. It is clear that the effectiveness of the catalyst on the basis of per unit of $\text{Co}(\text{OAc})_2$ decreases with metal loading. This may be caused by the increase of the relative amount of inaccessible metal centers when the metal loading increases.

3.3. Temperature effect on the autooxidation of cumene catalyzed by $\text{Co}(\text{OAc})_2\text{-BR-2.0}$

In Fig. 3, the oxygen consumption curves for cumene autooxidation in the presence of $\text{Co}(\text{OAc})_2\text{-BR-2.0}$ are shown as a function of temperature. When the reaction temperature decreases, induction period can be observed. At 323 and 333 K, the induction periods are about 0.5 h. At 343 K and above, no induction period was observed. The oxygen consumption rate decreases with temperature. It is noteworthy that the oxygen consumption rate depends slightly on the oxygen pressure. The rate slows down when the oxygen pressure decreases. This is in contrast with the $\text{Cu}(\text{OAc})_2\text{-CHX-0.6}$ [13] and $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$ [14] catalyzed reaction in which the oxygen consumption rates are independent of oxygen pressure when oxygen pressures are over certain threshold value. This threshold is approximately 30 kPa and increases with the amount of CHP for the autooxidation catalyzed by these two catalysts.

The results of product analyses are collected in Table 3. At a conversion of 7%, the selectivity of CHP decreases with temperature. It de-

creases steadily from 87.7% at 363 K to 68.2% at 323 K. This is unusual because in most catalytic reactions the side reaction is often suppressed with a decrease in the reaction temperature. A reasonable explanation is that the side reaction leading to PP has an activation energy lower than that leading to the desired product CHP. Under this condition, when temperature decreases, the rate for CHP formation slows down more than that for the side product PP formation. Therefore, the amount of CHP relative to PP is reduced at low temperature. The oxygen consumption rate also decreases with temperature, from 8.25×10^{-5} M/s at

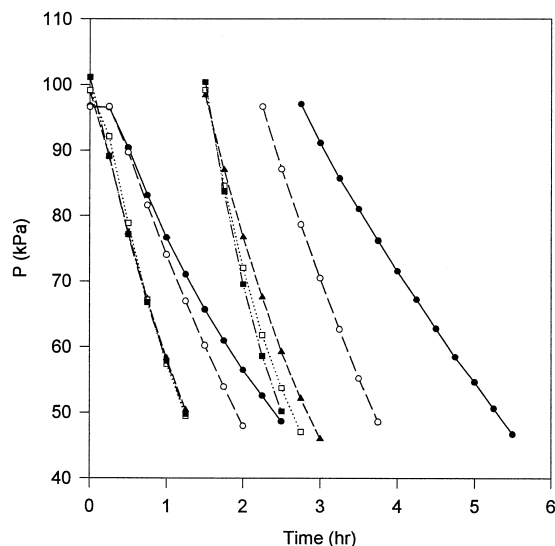


Fig. 3. The pressure of oxygen $P(\text{O}_2)$ ($V = 0.11$ l) as a function of reaction time in the autooxidation of cumene (10 ml) in the presence of $\text{Co}(\text{OAc})_2\text{-BR-2.0}$ (0.20 g) at various temperature: (●): 323 K, (○): 333 K, (▲): 343 K, (□): 353 K, (■): 363 K.

Table 3

Product distribution and rate of autooxidation of cumene (10 ml) in the presence of $\text{Co}(\text{OAc})_2\text{-BR-2.0}$ (0.20 g) at various temperatures; initial $P(\text{O}_2)$: 100 kPa ($V = 0.11$ l)

Temperature (K)	α (%)	$\Delta n(\text{O}_2)$ (mmol)	CHP (mmol)	PP (mmol)	S(CHP) (%)	Rate (10^{-5} M/s)
363	6.95	4.68	4.36	0.61	87.7	8.15
353	6.87	4.42	4.90	1.01	79.5	7.13
343	7.75	4.90	4.01	1.53	72.4	6.03
333	7.19	4.41	3.65	1.49	71.0	4.64
323	7.28	4.40	3.55	1.66	68.2	3.13

All notations are the same as specified in Table 1.

363 K to 3.13×10^{-5} M/s at 323 K. Therefore, for the $\text{Co}(\text{OAc})_2\text{-BR-2.0}$ catalyzed cumene autooxidation, it does not have any advantage to carry out the reaction at low temperature from the consideration of both the reaction rate and the selectivity to CHP. This conclusion may be hold for the autooxidation of other organic compounds to hydroperoxide catalyzed by a transition metal salt (see Section 3.5).

3.4. Comparison of the effectiveness of polymer supported and soluble copper carboxylate in catalyzing the autooxidation of cumene

From the dependence of the autooxidation reaction of cumene on MS-BR-0.6, we found that copper acetate is a good choice among the transition metal salts based on the consideration of both the reaction rate and the selectivity to CHP. To understand the effect of polymer support, we compared the catalytic activities of $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$ and soluble copper carboxylate salts: CuLu_2 (Lu: laurate, $\text{C}_{11}\text{H}_{23}\text{COO}^-$) and CuSt_2 (St: stearate, $\text{C}_{17}\text{H}_{35}\text{COO}^-$). In Fig. 4, a small amount of CuLu_2 or CuSt_2 are more effective in oxygen consumption than $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$. In contrast to $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$, no induction period was observed for the soluble $\text{Cu}(\text{II})$ carboxylates. The homogeneous catalysts also possess faster oxidation rates. The results of product analyses are shown in Table 4. In spite of using only about 20 μmol of soluble $\text{Cu}(\text{II})$ salt, the oxygen consumption rates is 2–3 times faster than that with

the polymer supported catalyst of 120 μmol $\text{Cu}(\text{OAc})_2$ in $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$. But the homogeneous catalytic systems have a selectivity to CHP only ca. 70%. This selectivity is inferior to that catalyzed by the polymer supported catalyst. Furthermore, in the homogeneous $\text{Cu}(\text{II})$ catalyzed reactions, acetophenone (AP) has been detected by ^1H NMR as indicated in Table 4. In both soluble and polymer supported catalysts, the copper(II) ions are coordinated by carboxylate anions. Therefore, a $\text{Cu}(\text{II})$ coordination sphere with carboxylate is not a sufficient condition in the copper catalyst to yield both a high autooxidation rate of cumene and a good selectivity to CHP.

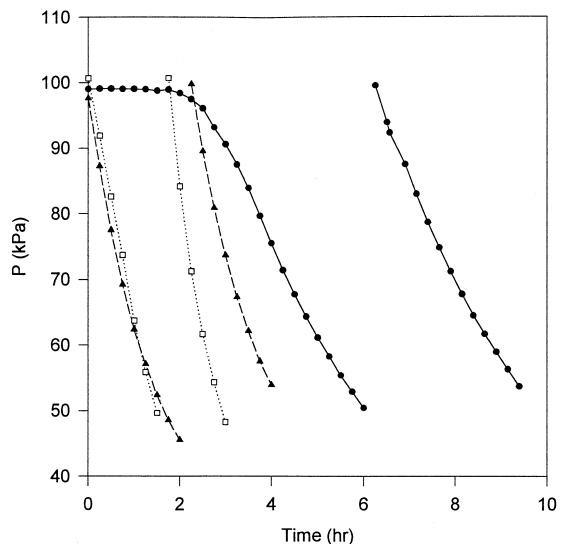


Fig. 4. At 363 K, the pressure of oxygen $P(\text{O}_2)$ ($V = 0.11$ l) as a function of reaction time in the autooxidation of cumene (10 ml) in the presence of catalyst; (●): $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$ (0.20 g) (data from Ref. [14]), (▲): CuLu_2 (9.6 mg), (□): CuSt_2 (11 mg).

Table 4

Product distribution and rate of the autooxidation of cumene (10 ml) in the presence of $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$ (0.20 g), or various homogeneous catalysts at 363 K; initial $\text{P}(\text{O}_2)$: 100 kPa ($V = 0.11$ l)

Catalyst	α (%)	$\Delta n(\text{O}_2)$ (mmol)	CHP (mmol)	PP (mmol)	AP ^a (mmol)	S(CHP) (%)	Rate (10^{-5} M/s)
$\text{Cu}(\text{OAc})_2\text{-BR-0.6}^b$	6.39	4.54	4.46	0.11	0	97.6	2.76
CuLu_2^c	6.74	4.21	3.57	1.06	0.19	74.1	5.02
CuSt_2^d	6.57	3.96	3.18	1.33	0.19	67.7	8.32

All notations are the same as specified in Table 1.

^aAP: acetophenone.

^bData from Ref. [14].

^c9.6 mg (21 μmol) copper(II) laurate.

^d11 mg (17 μmol) copper(II) stearate.

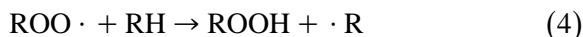
3.5. Mechanistic interpretation on the selectivity of CHP in cumene autooxidation catalyzed by transition metal salt supported on polymer

The mechanism of the autooxidation of cumene [16–18] can be described by the following equations:

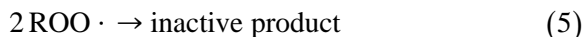
Initiation:



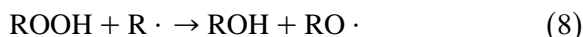
Propagation:



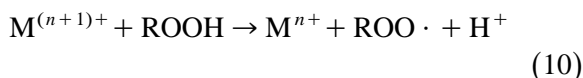
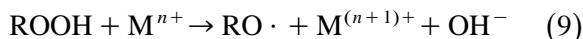
Termination:



Branching:



When the autooxidation reaction is catalyzed by a transition metal salt, additional reactions [19–22] are included in the mechanism



Eqs. (1) and (2) are the initiation mechanism for the thermal autooxidation. The presence of transition metal salt may catalyze the initiation reaction in Eq. (1). In addition, it can also

generate more radicals by the redox reactions in Eqs. (9) and (10). The radicals produced in Eqs. (9) and (10) can participate in the reactions in Eqs. (3)–(8) directly or after further reaction. Therefore, in general, the transition metal salt can catalyze the autooxidation of cumene. The absence of catalytic activity of Ni can be attributed to the inability of Ni(II) to participate in Eqs. (9) and (10). This is reasonable because both Ni(I) and Ni(III) are highly unstable [20]. The ineffectiveness of $\text{Cr}(\text{NO}_3)_3\text{-BR-0.6}$ may be attributed to the difficulty of Cr(III) to change its oxidation state. In $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$, $\text{M}^{(n+1)+}$ in Eqs. (9) and (10) is assigned to Cu(II), and M^{n+} is assigned to Cu(I). This assignment is based on the consideration that Cu(III) is inaccessible in this reaction because of this uncommon oxidation state. The reason that the $\text{Co}(\text{OAc})_2\text{-BR-0.6}$, $\text{Mn}(\text{OAc})_2\text{-BR-0.6}$ and $\text{FeCl}_2\text{-BR-0.6}$ supported catalysts have a high oxidation rate is that these metal ions have easily accessible +3 oxidation states. For these catalysts, the reactions in Eqs. (9) and (10) are very effective. Therefore, the radical concentration in the cumene autooxidation reaction medium is high when these catalysts are present. When $\text{Cu}(\text{OAc})_2$ is used as catalyst, the rate of radical buildup (reactions in Eqs. (9) and (10)) is moderate that lead to an autooxidation reaction rate that is faster than that initiated by CHP.

We carried out experiments to test the abilities of $\text{Co}(\text{OAc})_2\text{-BR-0.6}$ and $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$ in decomposing cumene hydroperoxide. We

added 0.1 g of each catalyst separately to two 5.0 ml cumene solution of 0.23 M in CHP under N_2 at 363 K. After 3-h reaction time, the concentration of CHP was measured to be 0.12 M for the CHP solution containing $Co(OAc)_2$ -BR-0.6. For the CHP solution containing $Cu(OAc)_2$ -BR-0.6, the concentration of CHP was 0.19 M after a 10-h reaction period. These results are consistent with our explanation that the buildup of radical concentration comes from the decomposition of CHP by the transition metal salt. Furthermore, these results also indicate that $Co(OAc)_2$ -BR-0.6 is more effective than $Cu(OAc)_2$ -BR-0.6 in decomposing CHP.

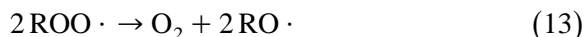
The mechanism for the cumene autooxidation in Eqs. (1)–(10) can also be used to explain the peculiar phenomenon that the selectivity of CHP in cumene autooxidation catalyzed by $Co(OAc)_2$ -BR-2.0 decreases with temperature. The rate determining step in CHP formation is the hydrogen abstraction in Eq. (4). This reaction involves the cleavage of a C–H bond, and is expected to have a high activation energy. When temperature decreases, the reaction rate of Eq. (4) reduced rapidly. However, the production of radicals from the redox reactions in Eqs. (9) and (10) is a low activation process in comparison with that of Eq. (4). Therefore, when temperature decreases, the reaction rate of Eq. (4) is reduced more than those of Eqs. (9) and (10). In other words, the rate of production of CHP slows down more rapidly than that of its decomposition. Therefore, in $Co(OAc)_2$ -BR-0.6 catalyzed autooxidation of cumene, the decrease of the selectivity of CHP with temperature can be satisfactorily accounted for. In general, the autooxidations of organic compounds follow the same mechanism as listed in Eqs. (1) and (10). The same reasoning given for cumene should also be applicable to other organic compounds. Therefore, we expect that the selectivity to organic hydroperoxide decreases with temperature in the autooxidations of organic compounds catalyzed by a transition metal salt.

In the cumene autooxidation to produce CHP, whether under the catalyzed or thermal condi-

tions, the major reaction side product is PP. This side product is produced mostly from the hydrogen abstraction reaction of alkoxy radical,



The alkoxy radical can be produced from the branching reaction in Eq. (8). This branching reaction is important when $R \cdot$ cannot react rapidly with O_2 when O_2 concentration is low or when there is an sufficient amount of ROOH. On the other hand, the termination reaction Eq. (5) can also lead to the formation of the alkoxy radical. Two pathways for the termination of two $ROO \cdot$ radicals have been established for tertiary peroxy radical [16–18].



Eq. (13) is the major pathway for the tertiary alkoxy radical. Therefore, both the termination reaction Eq. (5) and branching reaction Eq. (8) lead to the result that PP is the major side product. We have examined carefully the products in the 323 K reaction listed in Table 3. In the 1H NMR spectrum of the reaction mixture, there is no trace of ROOR, in confirmation to the significance of Eq. (13) relative to Eq. (12).

The redox potentials of the metal ions in the supported catalysts are greatly affected by their environments. But the different catalytic oxidation rates for various catalysts in Table 1 cannot be explained on the basis of the redox potential differences. This is because the redox potential is an equilibrium quantity whereas the oxidation rate is a kinetic quantity.

In the autooxidation of cumene catalyzed by soluble copper(II) carboxylates, the oxidation rates (Table 4) are about as fast as that catalyzed by MS-BR-0.6 (Table 1, MS = $Co(OAc)_2$, $Mn(OAc)_2$ and $FeCl_2$). However, the selectivity to CHP is poor. Therefore, Cu(II) catalytic center coordinated by carboxylate is not a sufficient condition for the polymer supported catalyst to be effective. The polymer support must contribute significantly to the behavior of $Cu(OAc)_2$ -BR-0.6. One possible ex-

planation is that when the metal ions change their oxidation states in Eqs. (9) and (10), the polymer support exerts some effect on this change of oxidation states. For the metal ions in $\text{Mn}(\text{OAc})_2\text{-BR-0.6}$, $\text{FeCl}_2\text{-BR-0.6}$ and $\text{Co}(\text{OAc})_2\text{-BR-0.6}$, the most common coordination numbers are six regardless of the oxidation states of metal ions being +2 or +3. Therefore, there is no major change of the coordination environments during oxidation state change for $\text{Co}(\text{OAc})_2$, $\text{Mn}(\text{OAc})_2$ and FeCl_2 on polymer support. The coordination number of $\text{Cu}(\text{II})$ is most likely 4 (square) or 5 [23]. On the other hand, the most common coordination number of $\text{Cu}(\text{I})$ is 4 (tetrahedral). The coordination number 3 is also common for $\text{Cu}(\text{I})$ as in hemocyanine and its model compounds [24–28]. Therefore, for copper salt catalyst, the oxidation state change in Eqs. (9) and (10), is accompanied with a major change of the coordination environment around copper center. In soluble copper salt, copper ion is free to adjust its coordination environment. On the contrary, in a polymer support, the adjustment is hindered by the polymer backbone. Therefore, polymer supported copper salt has a slow and effective rate of generating radicals by Eqs. (9) and (10). However, the hydroperoxide is not decomposed excessively in the presence of $\text{Cu}(\text{OAc})_2$ supported on Bio-Rex 70. Therefore, the selectivity to CHP is high. It becomes an effective catalyst for the cumene autooxidation to produce CHP. For $\text{Mn}(\text{OAc})_2\text{-BR-0.6}$, $\text{FeCl}_2\text{-BR-0.6}$ and $\text{Co}(\text{OAc})_2\text{-BR-0.6}$ catalysts, the reaction rates in Eqs. (9) and (10) are fast, therefore, the cumene autooxidation rate is fast and the selectivity to CHP is low.

4. Conclusion

From the results of cumene autooxidations in the presence of a series of transition metal salts supported on Bio-Rex at 363 K, we found that $\text{Cu}(\text{OAc})_2\text{-BR-0.6}$ is the best catalyst. This catalyst gives a fast autooxidation rate and a high

selectivity to CHP. The soluble copper(II) laurate or stearate catalyst can enhance the cumene autooxidation rate but it gives a poor selectivity to CHP. The major difference between the polymer supported and soluble $\text{Cu}(\text{II})$ catalytic center may be attributed to that in the polymer surrounding, the rate of redox decomposition of CHP is reduced by hindering the oxidation state change of copper center, whereas in soluble catalyst no such hindrance exists. We also found that in $\text{Co}(\text{OAc})_2\text{-BR-2.0}$ catalyzed autooxidation, the rate of oxidation decreases with temperature. However, unexpectedly, we found that the selectivity to CHP also decreases with temperature. This is attributed to that the formation of CHP has an activation energy higher than that of the catalyzed redox decomposition of CHP. Therefore, when temperature decreases, the rate of CHP formation is reduced more than that of CHP decomposition, leading to the observed trend in selectivity.

Acknowledgements

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