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Selective oxidation of 2-isopropylnaphthalene to 2-isopropylnaphthalenehydroperoxide in a gas–liquid reaction system using CuO+NaOH$_{aq}$ catalyst

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Abstract

The catalytic activities of CuO+NaOH$_{aq}$ and Cu_2O+NaOH$_{aq}$ in the liquid-phase selective oxidation of 2-isopropylnaphthalene (2-IPN) to 2-isopropylnaphthalenehydroperoxide (2-IPNHP) were compared, and the process parameters using CuO+NaOH$_{aq}$ catalyst were investigated. It was found that the atomic ratio of copper to sodium ions of the catalyst system affected the product distribution, a temperature 100°C was favourable for the selective production of 2-IPNHP, and the degree of back-mixing and liquid-phase mass transfer limitation markedly affected the conversion and selectivity. 2-IPNHP (1.254 mol dm^{-3}) was produced from 2-IPN (6.9 mol dm^{-3}) with 76% selectivity in a bubble column reactor with molecular oxygen as the oxidizing gas. An oxidation mechanism that depends on the unique combined catalytic behaviour of CuO+NaOH$_{aq}$ was proposed.

Keywords: 2-Isopropylnaphthalenehydroperoxide; 2-Isopropylnaphthalene oxidation; Product distribution and selectivity; Gas–liquid reaction with mass transfer limitation; Free-radical chain reactions

1. Introduction

The liquid-phase oxidations of alkylaromatics with air or molecular oxygen are commercially important reactions for the production of oxygenated compounds [1]. The production of hydroperoxides is the key step in hydrocarbon oxidation processes. This unstable intermediate is further oxidized to various end products that alter the selectivity. These products usually have acidic character and help to increase the decomposition of the hydroperoxide. The extent of the secondary oxidation and decomposition reactions can be minimized by using a selective oxidation catalyst, optimizing the reaction medium and conditions, considering mass transfer effects and controlling the system effectively [2].

The oxidation product of 2-isopropylnaphthalene (2-IPN), 2-isopropylnaphthalenehydroperoxide (2-IPNHP), is of industrial importance; it is the intermediate in the novel 2-naphthol and acetone process which includes alkylation, oxidation and decomposition subprocesses [3]. The oxidation details for some processes, i.e. for *p*-xylene, ethylbenzene, cumene and toluene oxidations to terephthalic acid, ethylbenzenehydroperoxide, cumenehydroperoxide and benzoic acid, respectively, can be obtained from the literature [1,4–7]. Limited information on the oxidation of 2-IPN can be found in the book by Topchiev et al. [8], and the first research results were reported by Takaç and Özdamar [9] and Boyacı et al. [10]. Decker et al. [11] submitted results related to selectivity in the stepwise oxidation of 2-IPN by oxygen and H_2O_2. Topchiev et al. [8] reported the oxidation of IPN in the presence of NaOH and $(CH_3)_3COOH$ at 84–92°C. Previously we have reported the reaction conditions, catalysts and kinetics for the alkylation of naphthalene to 2-IPN [12–14], and for the oxidation of 2-IPN to 2-IPNHP [9,10,12]. In our first paper on 2-IPN oxidation, the main features of the gas–liquid–solid/catalytic oxidation system in the presence of metallic copper were investigated, and a free-radical chain-reaction mechanism through the formation of a metal–oxygen complex was proposed [9]. In the following paper, we improved the catalytic reaction system by studying the influence of alkali on the conversion and selectivity, and showed the catalytic activities of NaOH, KOH and LiOH through the formation of Na_2O_2, KO_2 and LiO_2, respectively [10]. The main product of 2-IPN oxidation is 2-IPNHP; however, dimethyl-2-naphthylcarbinol

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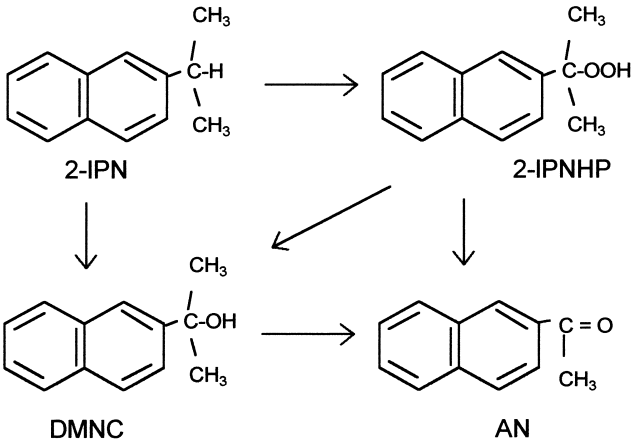

Fig. 1. Reaction pathway and molecular products of 2-IPN oxidation.

(DMNC) and 2-acetonaphthone (AN) can also be produced, depending on the reaction conditions. We achieved a concentration of 25.4% (w/v) of 2-IPNHP with 73% selectivity using $NaOH_{aq}$ at 110°C in a mechanically agitated gas–liquid/catalytic reactor [10]. The reaction pathway in terms of molecular products for the oxidation of 2-IPN is depicted in Fig. 1. In this paper, we report further investigations on the process conditions for the liquid-phase selective oxidation of 2-IPN to 2-IPNHP in the presence of copper oxides in alkali medium.

The mechanisms of alkylaromatic oxidation reactions are dependent on the catalyst. The effect of an initiator–catalyst can be explained mainly by the redox reactions of transition metals [6], by complex formation between the metal and oxygen or hydrocarbon [1] or through peroxide formation [15]. In this research, we used a transition metal and an alkali, which together produce unique effects different from those of the individual components. The catalytic activities of $CuO+NaOH_{aq}$ and $Cu_2O+NaOH_{aq}$ were compared, and the optimum process conditions for the liquid-phase selective oxidation of 2-IPN to 2-IPNHP were determined using $CuO+NaOH_{aq}$. The effects of the atomic ratio of copper to sodium ions of the catalyst system, temperature, oxidizing gas, gas feed rate and reactor configuration on the concentration and selectivity of 2-IPNHP were investigated. A free-radical chain-reaction mechanism for 2-IPN oxidation in the presence of $CuO+NaOH_{aq}$ was proposed.

2. Experimental details

The oxidation of 2-IPN was carried out in two different multiphase reaction systems consisting of temperature-controlled Pyrex reactors equipped with a thermometer, reflux cooler and gas inlet and sampling outlet ports. Mechanically agitated and bubble column (*L*/*D*=4) reactors with appropriate gas spargers were operated in semi-batch mode.

The reactant, 2-IPN, was produced as described elsewhere [13]. Molecular oxygen or air was used as the oxidizing gas. NaOH solution (5%, w/v) was used to make the reaction medium alkali and the oxidation was started after the removal of water from the NaOH solution. Cylindrical copper pieces ($0.4^{\Phi}\times 2$ mm) and a static cylindrical tube ($3^{\Phi}\times 11$ cm) made of copper wire (0.4^{Φ} mm) net were used in the mechanically agitated and bubble column reactors, respectively, after being washed in sequence with fuming nitric acid and water [16]. By air blowing at high temperature (1000°C), Cu_2O catalyst was prepared and placed into the reactor after the removal of water from the 2-IPN–$NaOH_{aq}$ emulsion. CuO was formed from Cu_2O within the reactor according to the following reactions which occur during the removal of water from the NaOH solution:

$$Cu_2O + 2H_2O + \tfrac{1}{2}O_2 \rightarrow 2Cu(OH)_2 \qquad (1)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \qquad (2)$$

These two types of catalyst system are abbreviated as $CuO+NaOH_{aq}$ and $Cu_2O+NaOH_{aq}$ in this study.

The concentration of 2-IPNHP was followed by iodometric titration [17], and the quantitative analyses of DMNC and AN were performed using a Fourier transform IR (FTIR) spectrometer (MIDAC) with ZnCe discs at wavenumbers of 3680 and 1682 cm^{-1}, respectively. An HP 5890 Model gas chromatograph (GC) was also used for the qualitative analysis of 2-IPN, DMNC and AN throughout the oxidations [16].

3. Results and discussion

3.1. Catalytic activities of $CuO+NaOH_{aq}$ and $Cu_2O+NaOH_{aq}$

Transition metals that exhibit more than one oxidation state are successively used in numerous hydrocarbon oxidations [6,7,18]. Takaç and Özdamar [9] reported the utilization of copper as catalyst in the oxidation of 2-IPN. Alkali metal ions also show catalytic activity in the oxidation of 2-IPN in addition to their neutralizing effect [10]. In this research, we investigated the catalytic activities of copper oxides in alkali medium.

The catalyst systems, which are abbreviated as $CuO+NaOH_{aq}$ and $Cu_2O+NaOH_{aq}$, showed different activities in the oxidation of 2-IPN. $Cu_2O+NaOH_{aq}$ produced more 2-IPNHP, DMNC and AN than was produced by $CuO+NaOH_{aq}$ (Fig. 2). However, the selectivity of 2-IPNHP (which is defined as the concentration of 2-IPNHP divided by the total concentration of the products) was higher for $CuO+NaOH_{aq}$ (Fig. 3). 2-IPNHP (1.321 mol dm^{-3}) with 65% selectivity and 2-IPNHP (1.049 mol dm^{-3}) with 75% selectivity were obtained from 2-IPN (6.9 mol dm^{-3}) by $Cu_2O+NaOH_{aq}$ and $CuO+NaOH_{aq}$, respectively. These results led us to choose $CuO+NaOH_{aq}$ as the catalyst for which we would determine the optimum process conditions.

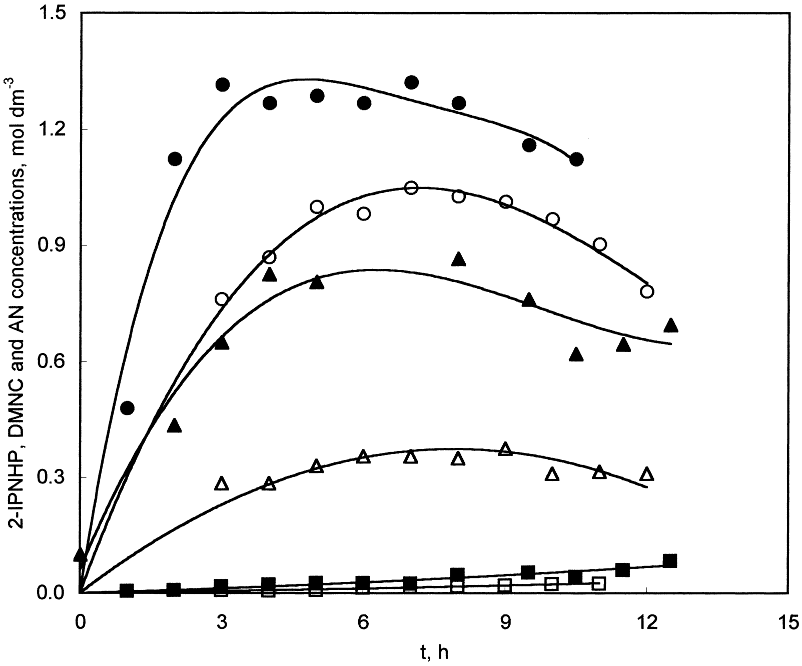

Fig. 2. Effects of CuO+NaOH$_{aq}$ and Cu$_2$O+NaOH$_{aq}$ on the 2-IPNHP, DMNC and AN concentrations. (T=110°C, Q_{O_2}=417 dm^3 dm^{-3} h^{-1}, N=1000 rpm, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated, Cu^{2+}/Na$^+$ atomic ratio=3.92×10^3.) CuO+NaOH$_{aq}$: (○) 2-IPNHP; (△) DMNC; (□) AN; Cu$_2$O+NaOH$_{aq}$: (●) 2-IPNHP; (▲) DMNC; (■) AN.

3.2. Effect of the Cu^{2+}/Na$^+$ atomic ratio of the CuO+NaOH$_{aq}$ catalyst

The effect of the Cu^{2+}/Na$^+$ atomic ratio of the CuO+NaOH$_{aq}$ catalyst on the production of 2-IPNHP and the product distribution was investigated at six values in the range 65–2×10^7, and the results are shown in Figs. 4–6. These ratios were calculated from the initial concentrations of copper and NaOH$_{aq}$ in the reactor. At low Cu^{2+}/Na$^+$ ratio (65), production of the byproducts rather than the hydroperoxide was observed. On increasing the ratio, the production of 2-IPNHP increased, and the DMNC and AN concentrations decreased. The 2-IPNHP concentration was high at Cu^{2+}/Na$^+$ atomic ratios between 1.96×10^3 and 1.57×10^4. At an atomic ratio of 1.57×10^4 more byproducts were produced than at ratios of 3.92×10^3 and 7.83×10^3. The 2-IPNHP and DMNC concentrations decreased, but the AN concentration increased when the ratio was increased from 1.57×10^4 to 2×10^7. These data show that both low and high concentrations of catalyst ions alter the product distribution in 2-IPN oxidation. In Fig. 7, the selectivity of 2-IPNHP (calculated at the maximum 2-IPNHP concentra-

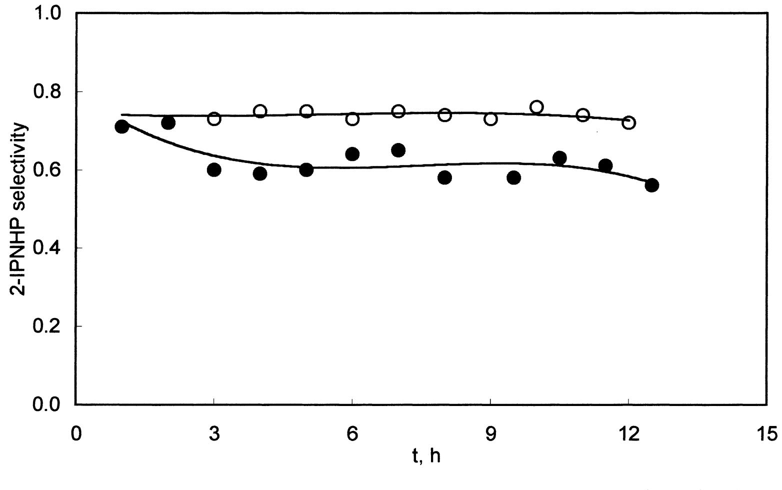

Fig. 3. Effects of CuO+NaOH$_{aq}$ and Cu$_2$O+NaOH$_{aq}$ on the 2-IPNHP selectivity. (T=110°C, Q_{O_2}=417 dm^3 dm^{-3} h^{-1}, N=1000 rpm, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated, Cu^{2+}/Na$^+$ atomic ratio=3.92×10^3.) Catalyst: (○) CuO+NaOH$_{aq}$; (●) Cu$_2$O+NaOH$_{aq}$.

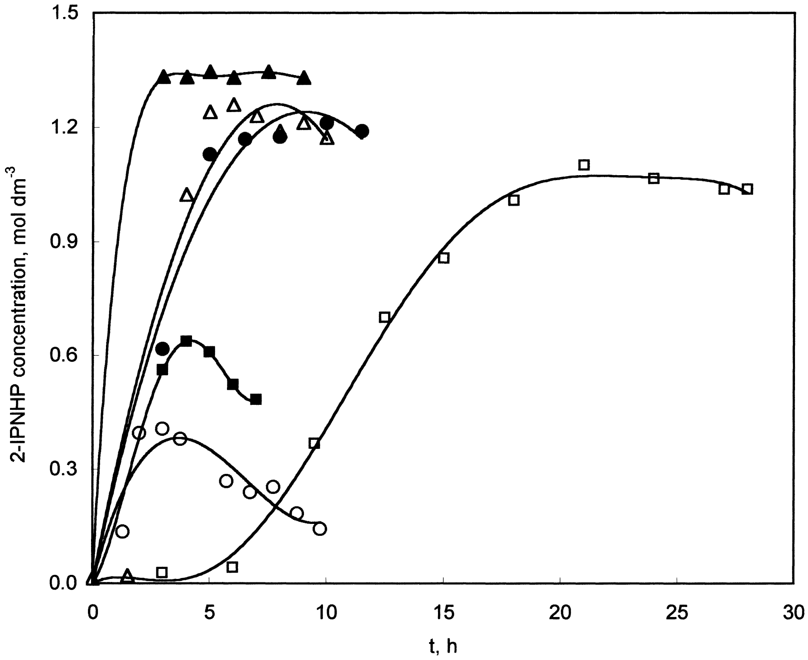

Fig. 4. Effect of the Cu^{2+}/Na^{+} atomic ratio on the 2-IPNHP concentration. (T=100°C, Q_{O_2}=417 $dm^3\ dm^{-3}\ h^{-1}$, N=1000 rpm, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated.) Cu^{2+}/Na^{+} atomic ratio: (■) 65; (▲) 1.96×10^3; (△) 3.92×10^3; (□) 7.83×10^3; (●) 1.57×10^4; (○) 2×10^7.

tion) is shown. Any Cu^{2+}/Na^{+} atomic ratio between 3.92×10^3 and 7.83×10^3 can be used for 2-IPNHP production with high selectivity. Although the selectivity is high at a Cu^{2+}/Na^{+} atomic ratio of 2×10^7, the 2-IPNHP concentration is low. As a result, a Cu^{2+}/Na^{+} atomic ratio of 3.92×10^3 is favourable in terms of both 2-IPNHP concentration and selectivity. 2-IPNHP (1.259 mol dm^{-3}) was obtained from 2-IPN (6.9 mol dm^{-3}) with 71% selectivity using CuO+$NaOH_{aq}$ catalyst at a Cu^{2+}/Na^{+} atomic ratio of 3.92×10^3.

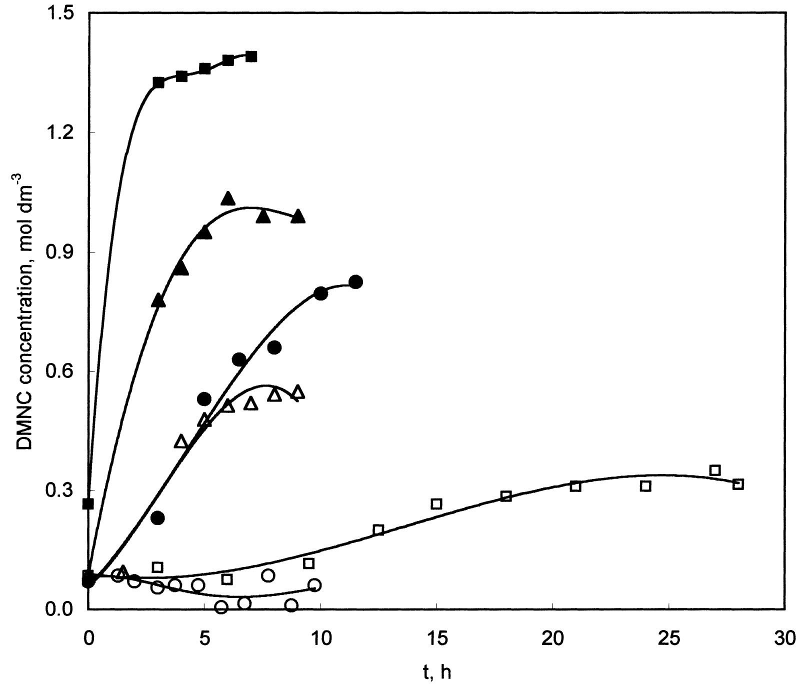

Fig. 5. Effect of the Cu^{2+}/Na^{+} atomic ratio on the DMNC concentration. (T=100°C, Q_{O_2}=417 $dm^3\ dm^{-3}\ h^{-1}$, N=1000 rpm, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated.) Cu^{2+}/Na^{+} atomic ratio: (■) 65; (▲) 1.96×10^3; (△) 3.92×10^3; (□) 7.83×10^3; (●) 1.57×10^4; (○) 2×10^7.

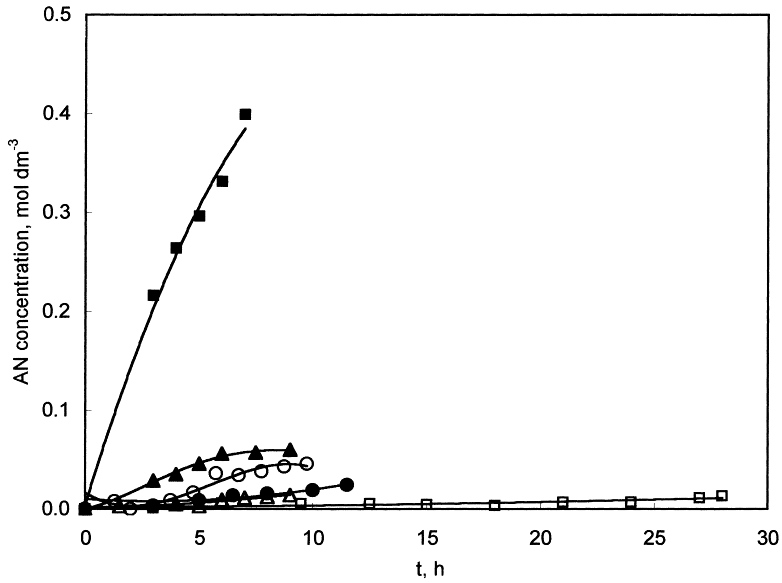

Fig. 6. Effect of the Cu^{2+}/Na^{+} atomic ratio on the AN concentration. (T=100°C, Q_{O_2}=417 $dm^3\ dm^{-3}\ h^{-1}$, N=1000 rpm, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated.) Cu^{2+}/Na^{+} atomic ratio: (■) 65; (▲) 1.96×10^3; (△) 3.92×10^3; (□) 7.83×10^3; (●) 1.57×10^4; (○) 2×10^7.

3.3. Oxidation mechanism of 2-IPN by $CuO+NaOH_{aq}$ catalyst

Hydrocarbon oxidations occur through free-radical chain-reactions, and the principal role of the oxidation catalyst is to produce the first radicals in the initiation period. The catalyst decomposes both the hydrocarbon and the hydroperoxide formed in the first period. Chain reactions are then propagated by the autocatalytic effect of the hydroperoxide [1]. In our first study, where the oxidation of 2-IPN was performed in the presence of metallic copper, we proposed a mechanism starting with the formation of an unsaturated metal–oxygen complex that produced the first radicals [9]. The mechanism of 2-IPN oxidation by $NaOH_{aq}$ which depends on the formation of Na_2O_2, was discussed in a previous paper [10]. In this study, however, we produced CuO from metallic copper according to Eqs. (1) and (2) and used it with $NaOH_{aq}$ in the oxidation. The presence of metal ions in the medium changes the oxidation mechanism, and the first radicals are formed both by redox reactions and through the formation of peroxide. The oxidation mechanism proposed for

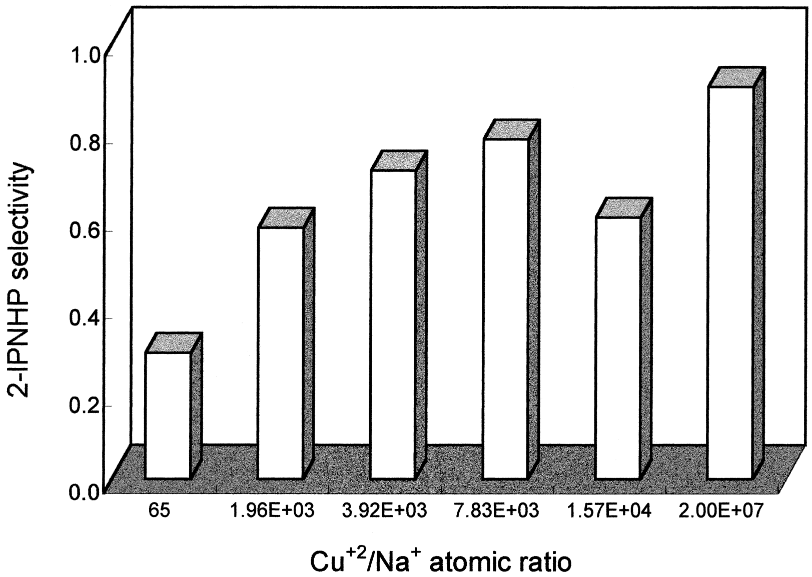

Fig. 7. Effect of the Cu^{2+}/Na^{+} atomic ratio on the 2-IPNHP selectivity. (T=100°C, Q_{O_2}=417 $dm^3\ dm^{-3}\ h^{-1}$, N=1000 rpm, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated.)

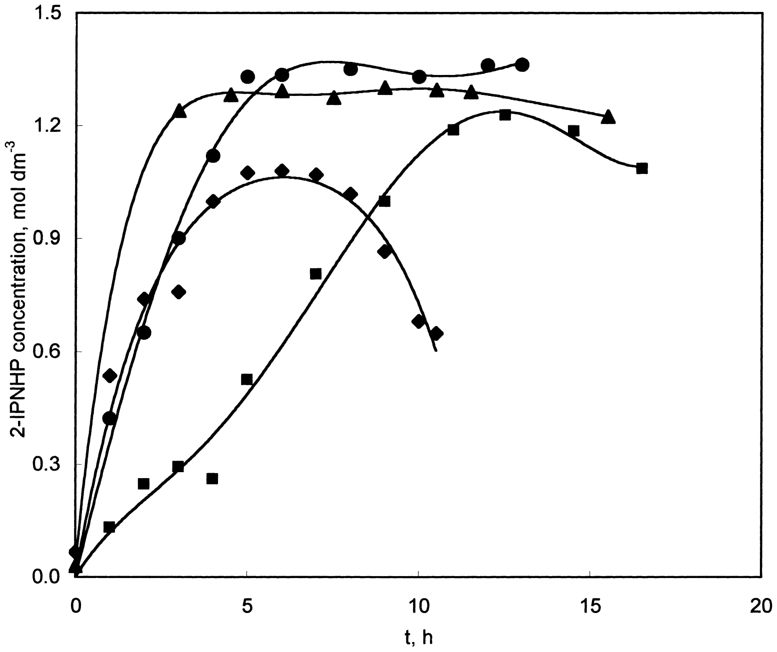

Fig. 8. Effect of temperature on the 2-IPNHP concentration. (Q_{O_2}=417 dm^3 dm^{-3} h^{-1}, N=1000 rpm, Cu^{2+}/Na$^+$ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated.) Temperature (°C): (▲) 90; (●) 100; (■) 110; (◆) 120.

the combined effect of Cu^{2+} and Na$^+$ ions is given in Appendix B.

3.4. *Effect of temperature*

The effect of temperature on the oxidation of 2-IPN was investigated at 90°C, 100°C, 110°C and 120°C. The 2-IPNHP and DMNC concentrations increased from 90°C to 100°C, but decreased at higher temperatures (Figs. 8 and 9). AN production increased with temperature (Fig. 9). Although the selectivity is slightly higher at 120°C than at lower temperatures (Fig. 10), 100°C is favourable for the oxidation of 2-IPN to 2-IPNHP due to the higher 2-IPNHP yield achieved.

3.5. *Effect of reactor configuration*

The reactor configuration affects the oxidation rate, conversion and product distribution. A plug flow reactor has the advantage of producing the intermediate hydroperoxide rather than the ultimate oxidation products. However, the oxidizing gas cannot be dispersed adequately within the liquid phase in a plug flow reactor, and the back-mixing regime is preferred for the production of radicals [2]. Efficient gas–liquid contact can be accomplished in mechanically agitated, bubble column or recycled reactors. We investigated the effect of reactor configuration on the oxidation of 2-IPN in semi-batch mechanically agitated and bubble column reactors where different degrees of back-mixing were provided. Because the interfacial area of a gas bubble in a mechanically agitated reactor is larger than that in a column reactor, the mass transfer between the phases is also different in the two reactors.

The oxidation performances of the reactors are shown as the variations in the 2-IPNHP, DMNC and AN concentrations and 2-IPNHP selectivity with residence time in Figs. 11 and 12, respectively. The same 2-IPNHP concentration was obtained in both reactors; however, the DMNC concentrations were different. There was little difference in the AN concentration. These results reveal a higher selectivity of 2-IPNHP in the bubble column reactor than in the mechanically agitated reactor, and make the bubble column reactor preferable for 2-IPN oxidation. The residence time required to reach the same 2-IPNHP concentration in the bubble column reactor is about three times larger than in the mechanically agitated reactor. However, the lower energy requirement and higher selectivity of the bubble column reactor make its use advantageous. 2-IPNHP (1.254 mol dm^{-3}) was obtained with 76% selectivity from 2-IPN (6.9 mol dm^{-3}) in the bubble column reactor, whereas 2-IPNHP (1.259 mol dm^{-3}) with 71% selectivity was obtained in the mechanically agitated reactor.

3.6. *Effect of oxidizing gas and gas feed rate*

The oxidation products are usually more reactive than the starting hydrocarbon. However, limiting the mass transfer between the phases can lessen the occurrence of secondary oxidations. A limitation in the gas or liquid phase of the contact of radicals with oxygen molecules decreases the

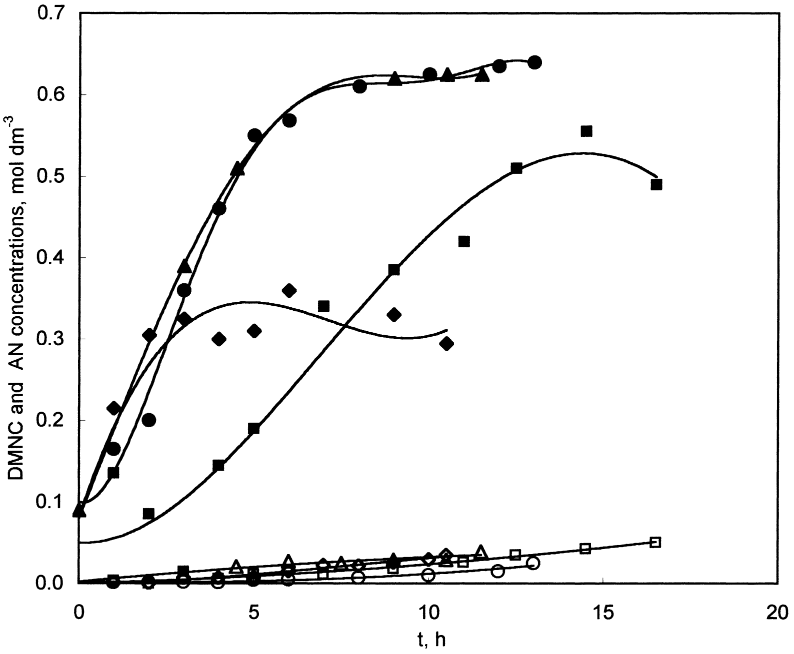

Fig. 9. Effect of temperature on the DMNC and AN concentrations. (Q_{O_2}=417 dm^3 dm^{-3} h^{-1}, N=1000 rpm, Cu^{2+}/Na$^+$ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated.) Temperature: 90°C: (▲) DMNC; (△) AN; 100°C (●) DMNC; (○) AN; 110°C: (■) DMNC; (□) AN; 120°C: (◆) DMNC; (◇) AN.

undesirable reactions. This limitation, nevertheless, should be made carefully so that an adequate concentration of desirable radicals is produced. The effect of the mass transfer resistance on the oxidation of 2-IPN in the gas and liquid phases was investigated in the bubble column reactor by using air instead of oxygen and by changing the gas feed rate, respectively. As the dissolved oxygen concentration was always high in the reaction medium, regardless of the oxidizing gas, the use of air was not expected to affect the reaction kinetics.

Fig. 13 shows that, when inert nitrogen gas limits the interaction of oxygen molecules with hydrocarbon, the initiation period increases considerably. However, the trend in the concentrations of the products shows that almost the same ultimate values would probably be achieved with both gases. Fig. 14 shows the same 2-IPNHP selectivity in both oxidations, indicating that the gas phase resistance does not affect the product distribution. The shorter initiation period makes the utilization of oxygen advantageous over air in further experiments.

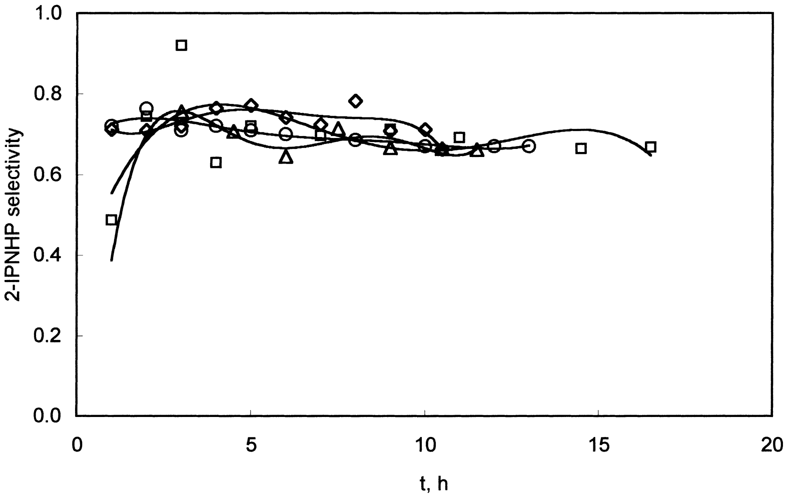

Fig. 10. Effect of temperature on the 2-IPNHP selectivity. Q_{O_2}=417 dm^3 dm^{-3} h^{-1}, N=1000 rpm, Cu^{2+}/Na$^+$ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}, reactor=mechanically agitated.) Temperature (°C): (△) 90; (○) 100; (□) 110; (◇) 120.

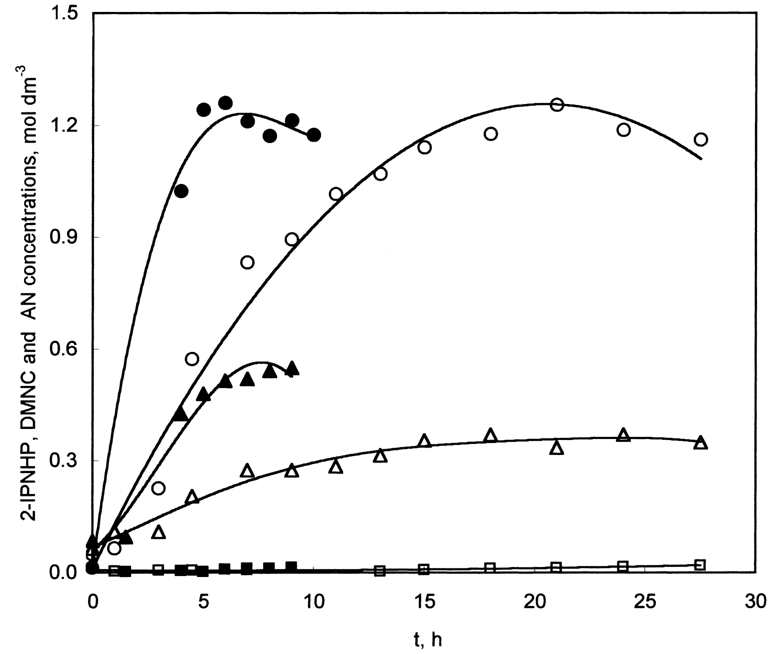

Fig. 11. Effect of the reactor configuration on the 2-IPNHP, DMNC and AN concentrations. (T=100°C, Q_{O_2}=417 dm^3 dm^{-3} h^{-1}, N=1000 rpm, Cu^{2+}/Na$^+$ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}.) Mechanically agitated: (●) 2-IPNHP; (▲) DMNC; (■) AN. Bubble column: (○) 2-IPNHP; (△) DMNC; (□) AN.

The oxidation of 2-IPN was performed under different liquid-phase mass transfer resistance conditions, which were created by changing the oxygen feed rate. An increase in the feed rate from 208 to 417 dm^3 dm^{-3} h^{-1} led to a decrease in the initiation period; however, the 2-IPNHP concentration obtained was almost the same at both feed rates. A further increment in the feed rate decreased the liquid-phase mass transfer resistance and consequently shortened the initiation period; however, the 2-IPNHP concentration achieved also decreased. Conversely, the byproduct concentrations were higher at 827 dm^3 dm^{-3} h^{-1} (Fig. 15). The effect of the liquid mass transfer resistance on the oxidation can also be seen in Fig. 16, which shows the variation of the 2-IPNHP selectivity with the oxygen feed rate. At 827 dm^3 dm^{-3} h^{-1}, the selectivity is lower than that at lower feed rates. These results indicate that efficient mass transfer in the liquid phase increases not only the oxidation rate of 2-IPN, but also the secondary oxidations. On the other hand, the removal of some liquid with the gas was observed at high feed rates.

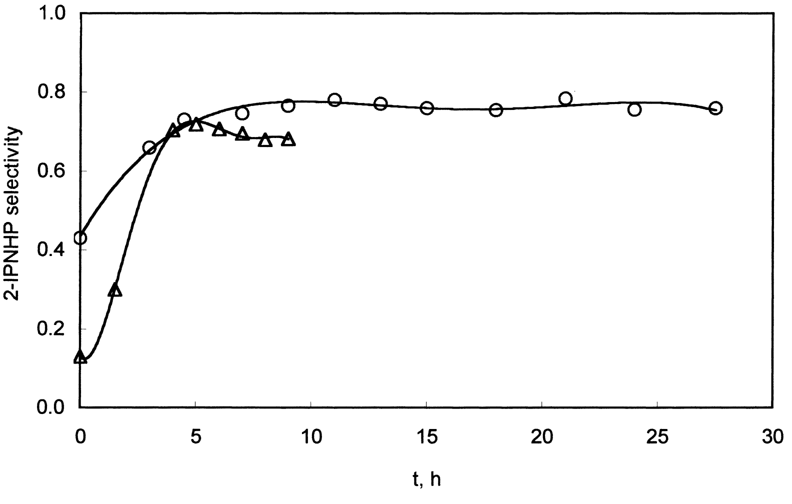

Fig. 12. Effect of the reactor configuration on the 2-IPNHP selectivity. (T=100°C, Q_{O_2}=417 dm^3 dm^{-3} h^{-1}, N=1000 rpm, Cu^{2+}/Na$^+$ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}.) Reactor: (△) mechanically agitated; (○) bubble column.

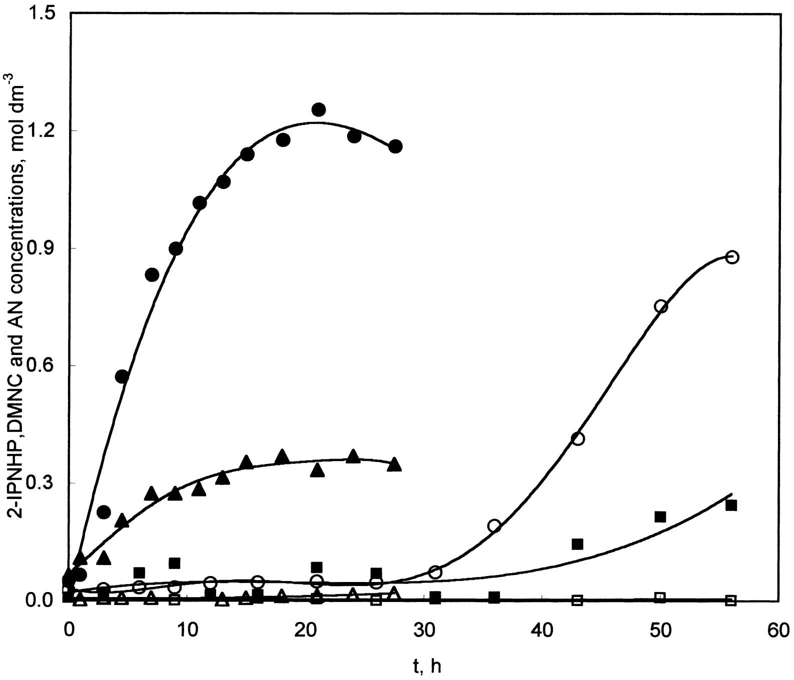

Fig. 13. Effect of the oxidizing gas on the 2-IPNHP, DMNC and AN concentrations. (T=100°C, Q=417 dm^3 dm^{-3} h^{-1}, Cu^{2+}/Na^+ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}, reactor=bubble column.) Oxygen: (●) 2-IPNHP; (▲) DMNC; (■) AN; Air: (○) 2-IPNHP; (△) DMNC; (□) AN.

4. Conclusions

The catalytic role of copper oxides in hydrocarbon oxidations is to generate free radicals by redox reactions. The activity of $NaOH_{aq}$, however, is through the formation of Na_2O_2 which initiates the chain reactions and yields 2-IPNHP [10]. We used copper oxides in different oxidation states in combination with $NaOH_{aq}$ in a two-component catalyst system in the oxidation of 2-IPN and compared the catalytic activities. Cu_2O gives redox reactions more easily than CuO as the since 2+ oxidation state of the metal is more stable. Therefore, we obtained a higher oxidation rate with $Cu_2O+NaOH_{aq}$ than with $CuO+NaOH_{aq}$. However, the high concentration of 2-IPNHP also induced its decomposition, and a lower selectivity of 2-IPNHP was observed with the $Cu_2O+NaOH_{aq}$ catalyst. Induced peroxide decomposition is shown in Eq. (B7) in the oxidation mechanism proposed. Furthermore, the stable catalyst $CuO+NaOH_{aq}$ was used for 275 h without losing any activity.

Although $NaOH_{aq}$ shows good activity in 2-IPN oxidation, at very high Na^+ concentrations, the 2-IPNHP production and selectivity are low because self-decomposition occurs [10]. When CuO and $NaOH_{aq}$ are combined, at low and high Cu^{2+}/Na^+ atomic ratios, the activities of Na^+ and Cu^{2+} ions are dominant, respectively. At very low Cu^{2+} concentration, the selectivity of 2-IPNHP is low

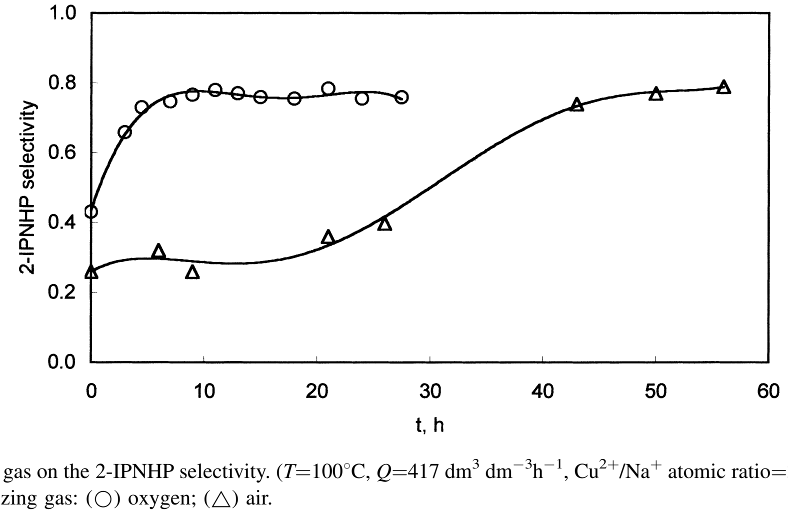

Fig. 14. Effect of the oxidizing gas on the 2-IPNHP selectivity. (T=100°C, Q=417 dm^3 $dm^{-3}h^{-1}$, Cu^{2+}/Na^+ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}, reactor=bubble column.) Oxidizing gas: (○) oxygen; (△) air.

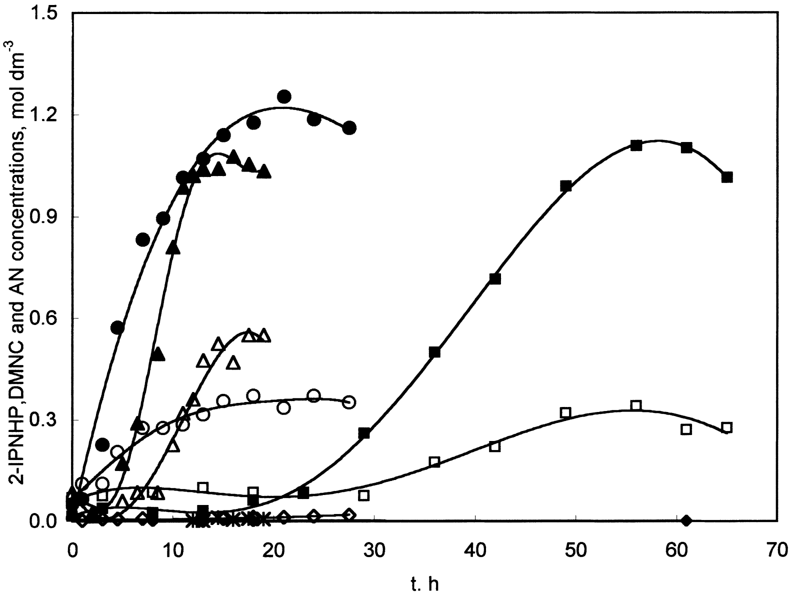

Fig. 15. Effect of the gas feed rate on the 2-IPNHP, DMNC and AN concentrations. (T=100°C, Cu^{2+}/Na^+ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}, reactor=bubble column.) Feed rate: 208 dm^3 dm^{-3} h^{-1}: (■) 2-IPNHP; (□) DMNC; (◆) AN; 417 dm^3 dm^{-3} h^{-1}; (●) 2-IPNHP; (○) DMNC; (◇) AN; 827 dm^3 dm^{-3} h^{-1}; (▲) 2-IPNHP; (△) DMNC; (*) AN.

and DMNC is the major product. More 2-IPNHP is produced with increasing Cu^{2+}/Na^+ atomic ratio, but, after a certain value has been reached, a slight decrease is observed. At very high Cu^{2+} concentrations, the production of 2-IPNHP, DMNC and AN is low, indicating the weak catalytic activity of Cu^{2+}. However, at the highest Cu^{2+}/Na^+ ratio, the AN concentration is high compared with the previous value. As a result, high Na^+ and Cu^{2+} concentrations lead to low 2-IPNHP production and there is a critical range of the Cu^{2+}/Na^+ atomic ratio in which the 2-IPNHP concentration and selectivity are both high.

In hydrocarbon oxidations, an increase in temperature is not always required because of the unstable character of hydroperoxides. We observed a maximum in the 2-IPNHP concentration with increasing temperature. As 2-IPNHP production decreases at temperatures higher than 100°C, this value is favourable for the selective oxidation of 2-IPN to 2-IPNHP. However, better oxidation progress can be achieved by working with an initial temperature of 120°C which provides more radicals, but 100°C at later stages of the oxidation to prevent the decomposition of 2-IPNHP.

The oxidation of 2-IPN with molecular oxygen in the presence of $CuO+NaOH_{aq}$ catalyst occurs in the liquid phase; however, mass transfer between the initial hydrocarbon and oxygen is necessary to produce the first radicals.

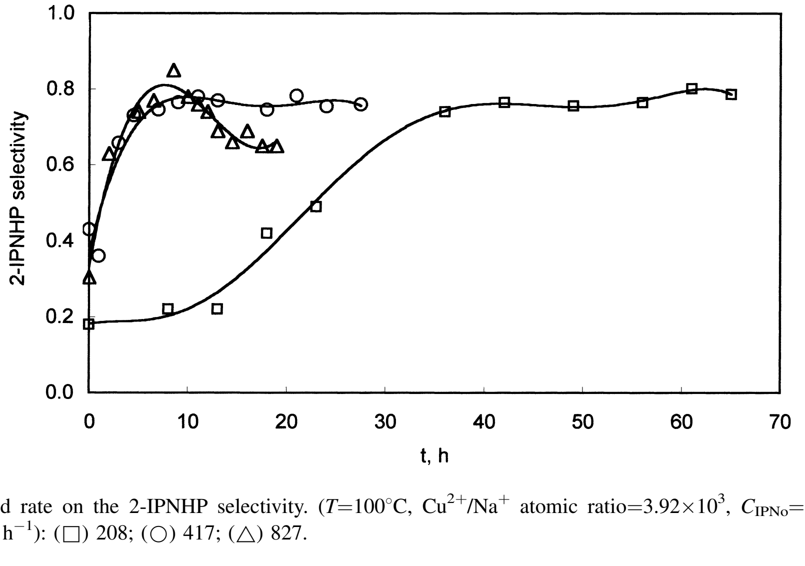

Fig. 16. Effect of the gas feed rate on the 2-IPNHP selectivity. (T=100°C, Cu^{2+}/Na^+ atomic ratio=3.92×10^3, C_{IPNo}=6.9 mol dm^{-3}, reactor=bubble column.) Feed rate (dm^3 dm^{-3} h^{-1}): (□) 208; (○) 417; (△) 827.

Therefore, oxidation can be controlled by the kinetics or by mass transfer. We oxidized 2-IPN in gas-phase and liquid-phase mass transfer controlled regimes.

The oxidations carried out using oxygen and air resulted in the same conversion and selectivity, indicating that the gas-phase mass transfer resistance does not prevent secondary oxidations. A smaller degree of back-mixing in conjunction with a low mass transfer efficiency, because of the small gas–liquid interfacial area in the bubble column reactor caused a weaker interaction of the hydrocarbon and oxygen molecules compared with that in the mechanically agitated reactor. By producing a small amount of 2-IPNHP and keeping its concentration low in the bubble column reactor, the self-decomposition of 2-IPNHP was prevented, and the oxidation route shifted mainly to 2-IPNHP production rather than secondary oxidations. A similar phenomenon was observed when there was a high liquid-phase mass transfer resistance at low oxygen feed rates. At a relatively high feed rate, where more efficient gas–liquid mass transfer was maintained by convection, the production of DMNC increased and the 2-IPNHP selectivity decreased. As a result, very efficient gas–liquid mass transfer is not desirable, and the liquid-phase mass transfer controlled regime is favourable for the selective oxidation of 2-IPN to 2-IPNHP.

Although a high mass transfer resistance provided by either a bubble column reactor or a low gas feed rate could increase the 2-IPNHP selectivity, the longer initial period of oxidation was a disadvantage. The slow reaction between the oxygen molecules and hydrocarbon due to insufficient mass transfer increased the initiation period. However, a decrease in the feed rate after achieving sufficient radical concentration may be a solution.

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Appendix A

Nomenclature

AN	2-acetonaphthone, $C_{10}H_7(CH_3)CO$
C	concentration, mol dm^{-3}
DMNC	dimethyl-2-naphthylcarbinol, $C_{10}H_7(CH_3)_2COH$
2-IPN	2-isopropylnaphthalene, $C_{10}H_7(CH_3)_2CH$
2-IPNHP	2-isopropylnaphthalenehydroperoxide, $C_{10}H_7(CH_3)_2COOH$
N	agitation rate, rpm
Q	gas feed rate, $dm^3\ dm^{-3}\ h^{-1}$
$R^\bullet$	isopropylnaphthyl radical, $C_{10}H_7(CH_3)_2C^\bullet$
RH	2-IPN
$RO^\bullet$	isopropylnaphthyloxy radical, $C_{10}H_7(CH_3)_2O^\bullet$
ROH	DMNC
$ROO^\bullet$	isopropylnaphthylperoxy radical, $C_{10}H_7(CH_3)_2OO^\bullet$
ROOH	2-IPNHP
ROOR	diisopropylnaphthylperoxide, $(C_{10}H_7(CH_3)_2C)_2O_2$
t	residence time, h
T	temperature, °C

Subscripts

aq	aqueous
o	initial value

Appendix B

Oxidation mechanism of 2-IPN by $CuO+NaOH_{aq}$ catalyst

Initiation period

$$RH + O_2 \rightarrow R^\bullet + HO_2^\bullet \tag{B1}$$

$$R^\bullet \rightarrow R^+ + e^- \tag{B2}$$

$$R^+ + OH^- \rightarrow ROH \tag{B3}$$

$$2Na^+ + O_2 + 2e^- \rightarrow Na_2O_2 \tag{B4}$$

$$RH + Na_2O_2 \rightarrow ROOH + 2Na^+ + 2e^- \tag{B5}$$

$$RH + HO_2^\bullet \rightarrow R^\bullet + H_2O_2 \tag{B6}$$

$$2ROOH \rightarrow ROO^\bullet + RO^\bullet + H_2O \tag{B7}$$

$$Cu^{2+} + Na_2O_2 \rightarrow Cu^+ + NaO_2 + Na^+ \tag{B8}$$

$$Na^+ + OH^- \rightarrow NaOH \tag{B9}$$

$$Cu^+ + Na_2O_2 \rightarrow Cu^{2+} + NaO^\bullet + NaO^- \tag{B10}$$

$$NaO^- + H^+ \rightarrow NaOH \tag{B11}$$

$$Cu^{2+} + NaO_2^\bullet \rightarrow Cu^+ + Na^+ + O_2 \tag{B12}$$

$$Cu^+ + NaO^\bullet \rightarrow Cu^{2+} + NaO^- \tag{B13}$$

$$NaO^\bullet + Na_2O_2 \rightarrow Na_2O + NaO_2^\bullet \tag{B14}$$

$$ROOH + Cu^{2+} \rightarrow Cu^+ + ROO^\bullet + H^+ \tag{B15}$$

$$ROOH + Cu^+ \rightarrow Cu^{2+} + RO^\bullet + OH^- \tag{B16}$$

Propagation period

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad (B17)$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \qquad (B18)$$

$$ROO^\bullet + Cu^{2+} \rightarrow R^+ + Cu^+ + O_2 \qquad (B19)$$

$$ROO^\bullet + Cu^+ \rightarrow ROO^- + Cu^{2+} \qquad (B20)$$

$$ROOH + R^\bullet \rightarrow ROH + RO^\bullet \qquad (B21)$$

$$RO^\bullet + Cu^+ \rightarrow RO^- + Cu^{2+} \qquad (B22)$$

$$ROOH \rightarrow RO^\bullet + OH^\bullet \qquad (B23)$$

$$RO^\bullet + RH \rightarrow R^\bullet + ROH \qquad (B24)$$

$$RO^\bullet \rightarrow AN + CH_3^\bullet \qquad (B25)$$

$$CH_3^\bullet + O_2 \rightarrow CH_3O_2^\bullet \qquad (B26)$$

$$CH_3O_2^\bullet + RH \rightarrow CH_2O + R^\bullet + H_2O \qquad (B27)$$

$$RH + OH^\bullet \rightarrow R^\bullet + H_2O \qquad (B28)$$

$$RO^- + H^+ \rightarrow ROH \qquad (B29)$$

$$R^+ + OH^- \rightarrow ROH \qquad (B30)$$

$$ROO^- + H^+ \rightarrow ROOH \qquad (B31)$$

$$ROO^- + Na^+ \rightarrow ROONa \qquad (B32)$$

$$ROOH + Na^+ \rightarrow ROONa + H^+ \qquad (B33)$$

$$ROOH \rightarrow ROO^- + H^+ \qquad (B34)$$

$$ROO^- + H_2O \rightarrow ROH + OOH^- \qquad (B35)$$

$$H^+ + OOH^- \rightarrow H_2O_2 \qquad (B36)$$

Termination period

$$2ROO^\bullet \rightarrow ROOR + O_2 \qquad (B37)$$

$$R^\bullet + ROO^\bullet \rightarrow ROOR \qquad (B38)$$

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