BIPHASIC SYNTHESIS OF α-TETRALONE USING NICKEL COMPLEX CATALYSTS

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Abstract – Organic-water interfacial autoxidation of tetralin was investigated using surface-active ligand complexes of transition metals (Cr, Ni, Mn, and Co) as catalysts, tetralin as the substrate and organic phase, and dodecyl sodium sulfate as an emulsifier. The major products formed under the experimental conditions of 60 °C and 1 atm were α-tetralone and α-tetralol, and the highest selectivity of 71 % to the desired product α-tetralone was achieved with nickel-tetraethylenepentamine complex. The optimum ligand to catalyst ratio was established to be 2 : 1 for the improved reaction rate and phase separation. The organic-water phase volume ratio around which the maximum reaction rate was attained was 2 : 1. The reaction order with respect to oxygen shifted from first to zero as its partial pressure increased, and the reaction order with respect to nickel catalyst concentration varied from 1.7 to 1, and subsequently to 0 with further increases in the metal concentration.

INTRODUCTION

Several studies employing the organic-water interfacial technique have been reported with promising results in carbonylation [Zhong et al., 1996], oxidative coupling [Dautenhahn and Lim, 1992; Zhong et al., 1996], and autoxidation [Ahn et al., 1997]. Biphasic catalytic reaction schemes in which a surface-active complexing agent or ligand is used to draw the catalyst to the organic-water interface where it effects the desired reaction can offer some significant advantages over conventional synthesis, homogeneous or heterogeneous reactions : These include (1) avoidance of the use of a toxic or environmentally troublesome solvent that may otherwise be needed, (2) catalyst recovery unaffected by the solubilities of the reactants and products in either aqueous or organic phase, (3) high reactivity, selectivity and reproducibility under mild reaction conditions, (4) ease of operation and control, (5) a higher solubility for a gaseous reactant than in an aqueous system, (6) a higher reaction rate due to the concentrating and intimate-contacting effects of the interface on the reactant(s) and catalyst, and (7) possibility of some stereoselectivity control on account of the directional influence of the interface [Lim and Zhong, 1996].

One of the functions of the complexing agent in the interfacial technique is to draw the catalyst to the organic-water interface, and therefore, surface affinity of the complexing agent is demanded. In the phase-transfer technique, on the other hand, surface affinity of the complexing agent only increases resistance to phase transfer, since the complexing agent would draw a reactant from one bulk phase to another (usually from aqueous to organic phase). In addition, the interfacial technique has much larger dispersed phase and greater capacity for holding the reactants in comparison with the micellar technique. Coalescence of the dispersed phase occurs spontaneously on standing, making phase separation and catalyst recovery easier. The interfacial technique is also different from the biphasic reaction method using a water-soluble ligand. With a water-soluble ligand, the catalyst is dispersed in the aqueous phase where the reaction is designated to occur unless the substrate has a low aqueous solubility and cannot be drawn into the aqueous phase by the use of a reverse phase-transfer agent. In summary, the interfacial synthesis technique can be viewed as an optimal hybrid of the micellar and phase-transfer techniques with respect to the interfacial area and the size of the dispersed phase. It combines a concentration-enrichment capability with a high substrate-holding capacity.

In this work, autoxidation of tetralin (1,2,3,4-tetrahydronaphthalene) to α-tetralone was studied using surface-active transition metal complex catalysts in a biphasic mode. Dehydrogenation of α-tetralone is a commercial process for the production of α-naphthol [Kamiya and Ingold, 1964; Mizukami and Imamula, 1978]. Since tetralin can serve as both organic phase and substrate in the biphasic autoxidation scheme, the recovery and recycle of the unreacted tetralin is greatly facilitated, and the use of such noxious and expensive solvents as acetic acid, chlorobenzene, or N,N-dialkylamide [Mizukami et al., 1979] can be avoided.

EXPERIMENTAL

The reaction was carried out in a batch mode at 1 atm in a 1,000 ml three-necked flask reactor using tetralin-water as the biphasic mixture, a transition metal complex of a surface-

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active ligand as the catalyst, and dodecyl sodium sulfate (DSS) as the emulsifier. The use of vigorous mechanical stirring and an anionic emulsifier (DSS) increased the dispersion lifetime and interfacial area of the reaction mixture and had a significant effect on the reaction rate.

A typical experimental run was carried out as follows : The reactor was charged with 100 ml of a 1 : 1 (by volume) tetralin-water mixture and the desired amount of DSS, surface-active ligand, and transition metal salt. The reactor was placed in a water bath and purged with oxygen for about 10 minutes and then allowed to equilibrate to the set temperature, which was typically 60 °C. After the reaction was initiated by starting the mechanical stirrer, the oxygen consumption for a given period was measured using a constant-pressure manometric unit.

After reaction was completed, the reaction mixture was emptied into a separating funnel and the organic and aqueous phase was separated out with an emulsion layer formed between the organic and aqueous phase upon standing overnight. The reaction products were analyzed using a SHIMADZU GC-14A gas chromatograph equipped with a CBP-20 capillary column.

RESULTS AND DISCUSSION

1. General Characteristics

Fig. 1 shows a representative oxygen uptake profile of a standard run. The reaction conditions for Fig. 1 are summarized in Table 1, and they correspond to the base runs upon which parametric variations would be made subsequently for ligand screening and detailed kinetic studies. With a suitable surface-active catalyst complex, such as tetraethylenepentamine complex of nickel, the reaction took off after an inductio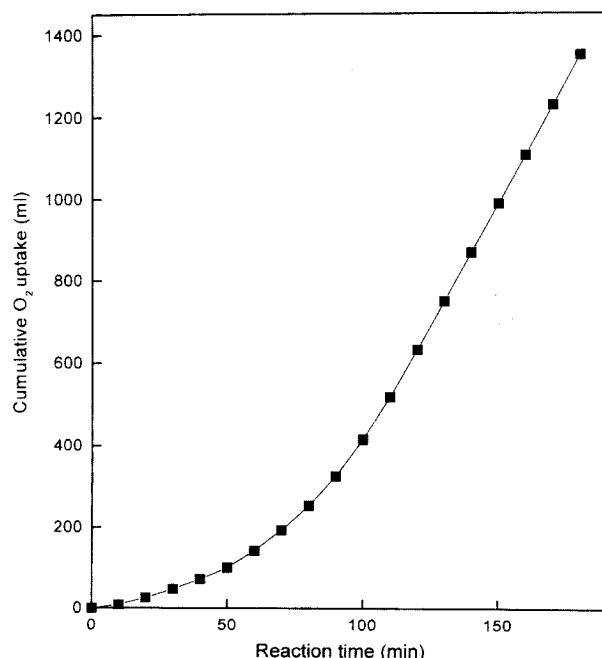n period. α-Tetralone and α-tetralol were the major reaction products irrespective of the metal and ligand used, and α-tetralyl hydroperoxide which has been reported as a major product in homogeneous reactions [Kamiya and Ingold, 1964; Mizukami and Imamula, 1978] was found to be negligible. It is believed that hydroperoxide formed in the immediate vicinity of the segregated metal complexes coupled with its amphiphilic character led to its decomposition [Ahn et al., 1997]. The higher oxidation products, i.e., α-naphthol and 1,2-dihydronaphthalene were detected only in a trace amount in an extended run. As the extent of reaction increased, a gradual change of color in the mixture was observed. Initially, the reaction mixture was opaque and white, but as the reaction time elapsed, a distinctive brown color of α-tetralone developed.

When the tetralin conversion level reached around 23 %, the organic phase underwent a phase inversion. The phase inversion was caused by the formation of α-tetralone and α-tetralol having a higher density (namely, 1.099 and 1.090 g/ml, respectively) than tetralin (0.973 g/ml). The formation of higher density products caused the organic phase to settle below the aqueous phase. The reaction stopped at a tetralin conversion of 35 % due to the build up of higher oxidation products that suppress the propagation chain of the reaction [Ahn et al., 1997]. Similar product inhibition has been reported in single-phase systems [Martan et al., 1970]. Presumably, these phenolic products inhibit the reaction by scavenging the free radicals involved in the autoxidation.

2. Results of Catalyst and Ligand Screening

The screening results on potential catalysts and ligands for the tetralin autoxidation are summarized in Table 2 and Table 3. In catalyst screening, the catalysts that had been known to promote the tetralin autoxidation reaction either homogeneously or heterogeneously--i.e., manganese, cobalt, chromium

Table 1. Standard reaction conditions for tetralin autoxidation

Kinetic parameter	Specification
Total pressure	760 mmHg
O_2 partial pressure	605 mmHg
Temperature	60 °C
Stirrer speed	1,500 rpm
Organic phase volume	50 ml
Aqueous phase volume	50 ml
Emulsifier & amount	DSS (Dodecyl Sodium Sulfate), 0.004 M
Catalyst & amount	$NiCl_2 \times H_2O$, 0.02 M
Ligand amount	TEPA (Tetraethylenepentamine), 0.04 M

Fig. 1. Cumulative O_2 uptake profile of autoxidation of tetralin.

Table 2. Results of catalyst screening in the biphasic autoxidation of tetralin[a]

Metal salt	O_2 uptake rate, M/h	α-Tetralone selectivity (%)
$CrCl_3$	0.415	54
$NiCl_2$	0.263	71
$Mn(Ac)_3$	0.638	48
$CoBr_2$	0.158	34

[a]Reaction conditions are the same as those specified in Table 1, except for the metal.

Table 3. Results of ligand screening in the biphasic autoxidation of tetralin[a]

Ligand	O_2 uptake rate, M/h	α-Tetralone selectivity, %	Induction period (min)
N,N'-Dimethylethylenediamine (DMEDA)	0.4104	65	90
N,N,N',N'-Tetramethylethylenediamine (TMEDA)	0.246	62	30
N,N-Dibutylethylenediamine (DBEDA)	0.018	33.3	-
N,N,N',N'-Tetraethylethylenediamine (TEEDA)	Negligible	-	-
N,N-Dibenzylethylenediamine (DBZNEDA)	Negligible	-	-
N,N,N',N'-Tetraethyldiethylenetriamine	0.008	22.7	-
Tetraethylenepentamine (TEPA)	0.263[b]	71	30
Triethyl phosphite	Negligible	-	

[a]Reaction conditions are the same as those specified in Table 1, except for the ligand.
[b]0.36 M/h at ligand-catalyst ratio of 1 : 1.

and nickel--were tested. Though the reaction rate catalyzed by nickel was slower than that with manganese or chromium, the highest α-tetralone selectivity was obtained in the nickel-catalyzed reaction. It is noteworthy that a high α-tetralone selectivity is commercially desirable, since α-tetralone can be more easily and directly converted to α-naphthol than α-tetralol, and in this respect, tetraethylenepentamine (TEPA) was the most effective among the ligands tested; the selectivity of α-tetralone was 71% with nickel-TEPA complex. Furthermore, when the ligand to catalyst ratio was changed from 2 : 1 to 1 : 1, its steady state oxygen uptake rate increased from 0.263 to 0.36 M/h. Though it was reported that long-chain primary amines were less effective as complexing agents, owing to their low aqueous solubility which causes metal to be precipitated out of the aqueous solutions as metal hydroxide [Lloyd et al., 1989], it appears that this problem is not serious in the case of TEPA which has an additional three secondary a-mine groups. The reaction using N,N'-dimethylethylenediamine (DMEDA), though its oxygen uptake rate was nearly 1.5 times faster than that with TEPA, led to lower α-tetralone selectivity of 65% followed by N,N,N',N'-tetramethylethylenediamine (TMEDA) with oxygen uptake rate of 0.246 M/h and α-tetralone selectivity of 62%. Primary and secondary amines can undergo oxidation to imines via elimination of hydrogen from the α-carbon, and for this reason tetramethylethylenediamine is often used in place of ethylenediamine with metals which are oxidizing agents [Collman et al., 1987].

The induction period was almost independent of nickel concentration regardless of the ligand used. The induction periods of the reactions with both nickel-TEPA complex and nickel-TMEDA were approximately thirty minutes. In the case of DM-EDA, though the induction period was longer, i.e., about ninety minutes, the steady-state oxygen uptake rate immediately following the induction period was faster than that with TEPA.

3. Detailed Kinetic Results

3-1. Rate Dependence on the Catalyst Concentration and Oxygen Partial Pressure

The variation of the steady state oxygen uptake rate with respect to catalyst concentration is shown in Fig. 2. The reaction order with respect to nickel catalyst concentration varied from 1.7 to 1, and subsequently to 0 with further increases in the metal concentration. The corresponding reaction in one-liquid-phase systems is reported to show a limiting order of 0.5 or 1.0 with respect to catalyst concentration [Guan et al.,
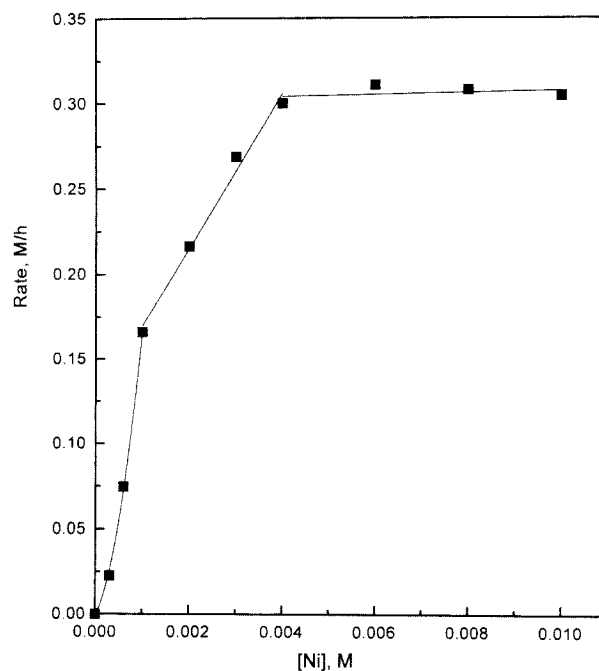

Fig. 2. Rate dependence on [Ni] concentration for the biphasic autoxidation of tetralin.

1980]. A variable reaction order with respect to catalyst concentration with a limiting value greater than unity is unusual, and this may be a unique feature of the biphasic autoxidation reactions.

Fig. 3 shows the effect of oxygen partial pressure on the biphasic autoxidation reaction. In contrast to one-liquid-phase systems in which rate dependence on oxygen partial pressure was mostly first order over a much wider pressure range [Guan et al., 1980; Zho et al., 1980], in the biphasic reaction the reaction order with respect to oxygen partial pressure shifted from first to zero order above an oxygen partial pressure of about 0.15 atm. The zero order rate dependence on the dissolved gas concentration under atmospheric conditions seems to be a feature of biphasic reactions [Zhong et al., 1995, 1996; Ahn et al., 1997]. The segregation of surface-active catalyst complex and its ability to absorb the gaseous reactant may create a localized high concentration of the dissolved gas a-round the organic-water interface, where the reaction occurs. As a consequence, it appears that the pressure requirement
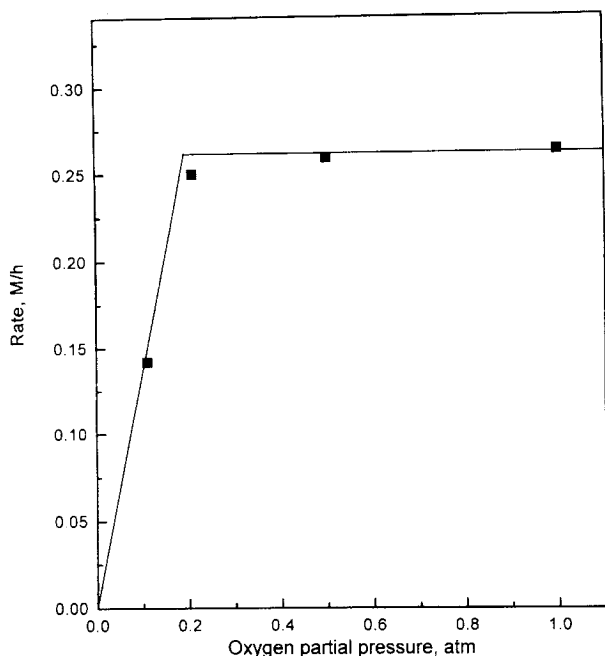
Fig. 3. Rate dependence on oxygen partial pressure for the biphasic autoxidation of tetralin.

of dissolved gaseous reactants may be substantially reduced in the biphasic reaction mode.

3-2. The Effects of Ligand-Catalyst Ratio

The effect of ligand-catalyst ratio on the reaction rate and α-tetralone selectivity is shown in Fig. 4. Ligand-catalyst ratio is expected to influence the reaction at the organic-water interface via two competing factors : a greater ability to position the catalyst at the O-W interface, and a lower accessibility of the reactants to the coordination sites of the catalyst
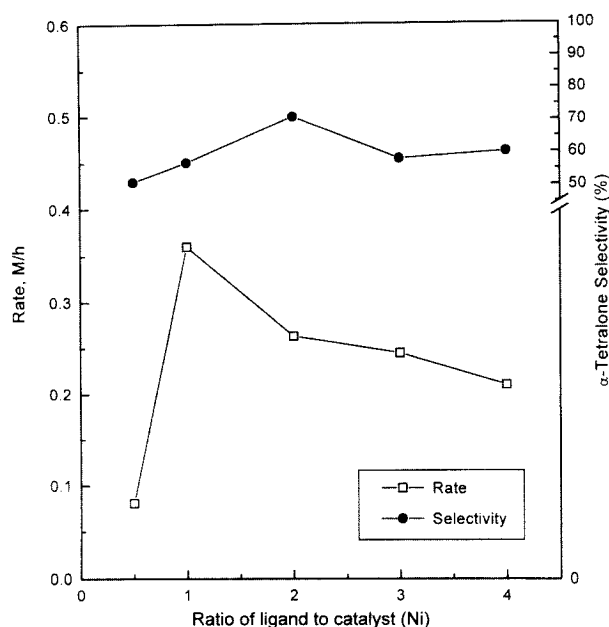
at increasingly higher ligand-catalyst ratios. α-Tetralone selectivity was a little higher around 2 : 1 ligand-catalyst ratio and the fastest rate was found to be around 2 : 1 with TEPA. The ligand-catalyst ratio also has shown effects on the phase separation.

3-3. The Effects of Organic-Water (O-W) Volume Ratio and Emulsifier

Interfacial reactions are strongly governed by the interfacial area and this in turn may be influenced by such parameters as organic-water volume ratio and the degree of emulsification. Because organic liquids generally have higher solubilities for gases than water, the existence of an organic phase can significantly increase the solubility of a gaseous reactant and lead to faster reaction rate. A greater dispersion shapes a finer emulsion that can hold more reactants in the active region and provide a larger interfacial area and a shorter diffusion path length for the reactants and catalyst complex [Lim and Zhong, 1996].

The effect of organic-water (O-W) volume ratio on the reaction rate and α-tetralone selectivity is shown in Fig. 5. The organic-water (O-W) volume ratio around which the maximum reaction rate was attained was found to be 2 : 1. α-Tetralone selectivity, however, was almost independent of the O-W ratio.

The result of emulsifier screening is shown in Table 4. The reaction with an anionic surfactant (DSS) showed much higher reaction rate than without it, while cationic (cetyltrimethylammonium bromide) or neutral (nonylphenol ethoxylates) surfactant types all resulted in a significant rate reduction. It appears that the anionic surfactant stabilized the positively charged catalyst complex at the interface and promoted the reaction rates. The dependence of reaction rate and α-tetralone selectivity on the emulsifier (DSS) concentration is shown in Fig. 6. As the emulsifier (DSS) concentration increased, the reaction rate increased very sharply and then leveled off above 0.015
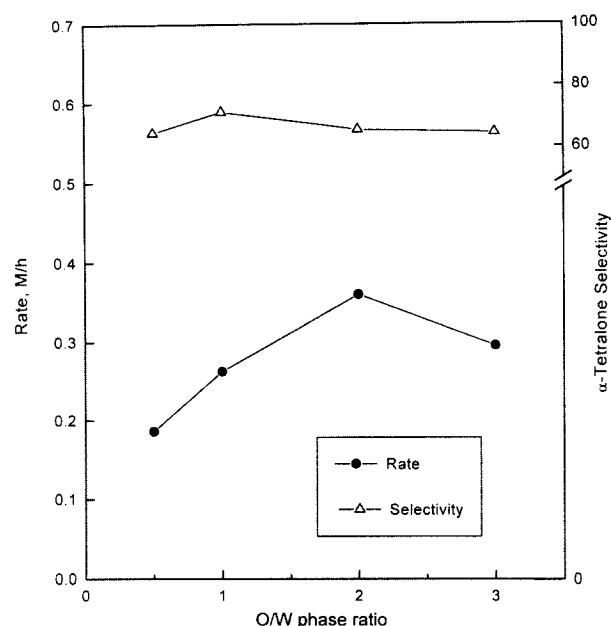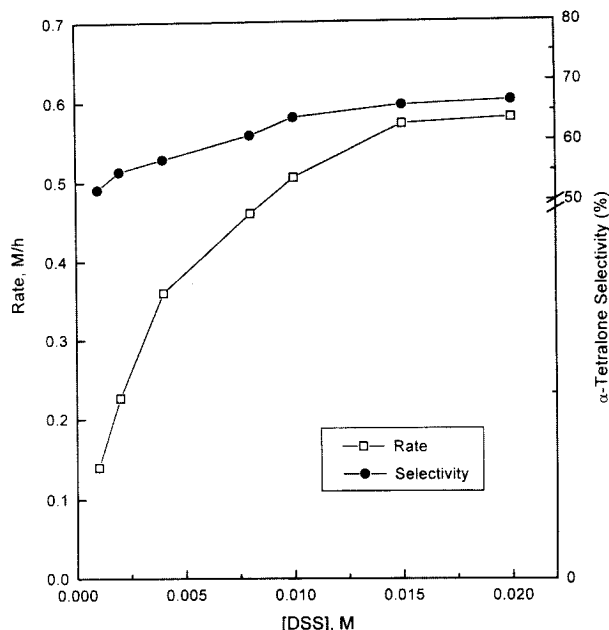

Fig. 4. The dependence of rate and α-tetralone selectivity on the ligand to catalyst ratio.

Fig. 5. The dependence of rate and α-tetralone selectivity on the organic-water (O-W) phase volume ratio.

Table 4. Effects of different emulsifiers in the biphasic autoxidation of tetralin^a

Emulsifier	O_2 uptake rate, M/h
Dodecyl sodium sulfate	0.263
Cetyltrimethylammonium bromide	Negligible
Nonylphenol ethoxylates (NP+9EO)	0.002
Without emulsifier	0.0045

^{a}Reaction conditions are the same as those specified in Table 1, except for the emulsifier.

Fig. 6. The dependence of rate and α-tetralone selectivity on the emulsifier (DSS) concentration.

Fig. 7. The rate dependence on the reaction temperature.

M. α-Tetralone selectivity showed a mild enhancement with DSS concentration, but again was almost independent above 0.015 M.
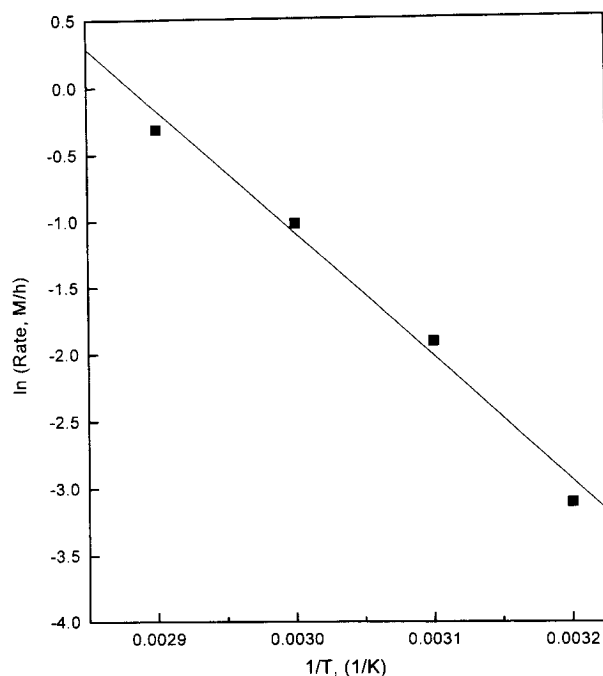
3-4. Rate Dependence on the Reaction Temperature

The temperature effect on the tetralin autoxidation over 40-70 °C range is presented in Fig. 7. According to this Arrhenius plot, the activation energy was estimated to be approximately 18.3 kcal/mol, which is sufficiently high to exclude the possibility of the reaction being limited by oxygen mass transfer.

4. Phase Separation and Segregation of Catalyst Complex at the O-W Interface

It was established that the ease of phase separation after the reaction was terminated was influenced by several factors: catalyst concentration, tetralin conversion, surface-activity of a ligand, ligand-catalyst ratio, type and amount of the emulsifier used in the reaction.

As catalyst concentration and tetralin conversion increased, the time needed for the phase separation decreased progressively; however, in the reaction with some ligands, N,N-dibutylethylenediamine or N,N,N',N'-tetraethyldiethylenetriamine, the phase separation took more than one week or the mixture was not separated even after one month. To segregate metal complex in the interface effectively, ligands used in the biphasic reaction should be complexing agents with

strong amphiphilic character to provide the driving force that pulls organic and water molecules towards them. The attributes of satisfactory ligands are known as follows: 1) easy accessibility to the coordinating center, 2) chelating ability, and 3) a compact umbrella-like structure [Lim and Zhong, 1996; Lloyd et al., 1989]. Presumably, an umbrella-like structure increases surface affinity by making it possible for the ligand to "float" at the organic-water interface.

The ligand-catalyst ratio was also found to affect the degree of phase separation. In the case of TEPA, within the ligand-catalyst ratio of 1 to 4, the separation time was reasonably short. At the ligand-catalyst ratio of 0.5, however, separation proceeded very slowly and, furthermore, metal was found precipitated. If the ligand concentration is not high enough to form a complex with metal to a sufficient extent, it can be difficult to draw metals to the interface.

Depending on the emulsifier types used, the occurrence of the phase separation was different. For the reaction mixture in which an anionic emulsifier was used, the phase separation occurred clearly and fast. On the other hand, in the cases of cationic or nonionic surfactants, the phase separation hardly occurred.

Once an emulsion layer emerged at the interface upon standing overnight after the completion of the reaction, the catalyst complex could be quantitatively recovered and it could be reused with no apparent loss of activity.

CONCLUSION

Autoxidation of tetralin was studied in a biphasic synthesis mode using a surface-active ligand complexes of transition metals as catalyst, tetralin as the substrate and organic phase, and dodecyl sodium sulfate as emulsifier. The organic-water

interfacial reaction scheme can provide several important advantages such as avoidance of using troublesome solvent, ease of catalyst recovery and substrate recycle. The main products of the reaction were α-tetralone and α-tetralol independent of catalyst complexes used. The α-tetralone selectivity was 71 % with a tetraethylenepentamine complex of nickel. The reaction order with respect to oxygen shifted from first to zero order as its partial pressure increased and the reaction order with nickel catalyst concentration varied from 1.7 to 1, and subsequently to 0 with further increases in the metal concentration.

An optimum ligand-catalyst ratio of 2 : 1 was obtained and the ligand-catalyst ratio had some effect on the ease of phase separation after reaction was stopped. The organic-water phase ratio around which the maximum reaction rate was attained was 2 : 1.

REFERENCES

Ahn, W. S., Zhong, Y., Adams, C. F. and Lim, P. K., "Biphasic Autoxidation of Tetralin Catalyzed by Surface-Active Transition Metal Complexes", *J. Phys. Chem. B*, **101**, 596 (1997).

Collman, J. P., Hegedus, L. S., Norton, J. R. and Finke, R. G., "Principle and Applications of Organotransition Metal Chemistry", University Science Books, Mill Vally, California (1987).

Dautenhahn, P. C. and Lim, P. K., "Biphasic Synthesis of Poly (2,6-dimethyl-1,4-phenylene oxide) Using a Surface-Active Coupling Catalyst", *Ind. Eng. Chem. Res.*, **31**, 463 (1992).

Guan, Y., Zhang, Z. and Zhou, J., "Studies on the Liquid-Phase Oxidation of Tetralin. I. Reaction Kinetics", *Ranliao Huaxue Xuebao*, **8**(1), 62 (1980); *Chem. Abstr.*, **96**, 6331n (1982).

Kamiya, Y. and Ingold, K. U., "The Metal-Catalyzed Autoxidation of Tetralin. III. Catalysis by Manganese, Copper, Nickel, and Iron", *Can. J. Chem.*, **42**, 1027 (1964).

Lim, P. K. and Zhong, Y., "Chemically Benign Synthesis at Organic-Water Interface", in Green Chemistry-Designing Chemistry for the Environment, edited by Paul Anastas and Tracy Williamson, ACS Symposium Series No. 626, American Chemical Society: Washington, DC, 168 (1996).

Lloyd, P. B., Ganesan, S. and Lim, P. K., "Segregation of Metals at the Oil-Water Interface: Results and Implications." *Ind. Eng. Chem. Res.*, **28**, 577 (1989).

Martan, M., Manassen, J. and Vofsi, D., "Oxidation of Tetralin, Tetralol and α-Tetralone. Dependence of Alcohol to Ketone Ratio on Conversion", *Tetrahedron*, **26**, 3815 (1970).

Mizukami, F., Horiguchi, Y., Tajima, M. and Imamura, J., "The Liquid-Phase Oxidation of Hydrocarbons with Molecular Oxygen. II. A Highly Selective Formation of α-Tetralone by the Metal-Catalyzed Oxidation of Tetralin in the Presence of N,N-Dialkylamides", *Bull. Chem. Soc. Jpn.*, **52**, 2689 (1979).

Mizukami, F. and Imamula, J., "Liquid-Phase Oxidation of Hydrocarbons with Molecular Oxygen. I. The Effects of Metal Ions Their Ligands on Product Distribution in the Oxidation of Tetralin in Acetic Acid", *Bull. Chem. Soc. Jpn.*, **51**, 1404 (1978).

Zhong, Y., Adams, C. F. and Lim, P. K., "Biphasic Synthesis of Poly(2,6-dimethyl-1,4-phenylene oxide) Using a Surface-Active Coupling Catalyst. 2. Process Improvements, Additional Kinetic Results, and Proposed Reaction Mechanism", *Ind. Eng. Chem. Res.*, **34**, 1529 (1995).

Zhong, Y., Godfrey, V. M., Brown, P. and Lim, P. K., "Biphasic Synthesis of Phenylacetic and Phenylenediacetic Acids by Interfacial Carbonylation of Benzyl Chloride and Dichloro-p-xylene", *Chem. Eng. Sci.*, **51**, 757 (1996).

Zhou, J., Zhang, Z. and Yude, G., "Studies on the Liquid-Phase Oxidation of Tetralin. II. Continuous Process and Reaction under Pressure", *Ranliao Huaxue Xuebao*, **8**(1), 71 (1980); *Chem. Abstr.*, **96**, 6332 (1982).