noanthracene ϕ_{ex} to be increased by 62% upon the addition of CTAB.

This means that the complex (XF) results in higher yield of excited state (F^*) of 1-aminoanthracene but lower excited state yield of anthracene in the presence of surfactants than those in the absense of surfactants, respectively. The cause of this opposite trend of ϕ_{ex} in the presence of surfactants is not clear at the present, but is speculated that surfactants affect the recombination process of the radical ions which are produced *via* electron transfer described as[12]

$$X + F \longrightarrow [X \dot{-} ---F \dot{+}] \longrightarrow F^* + \text{products} \qquad (4)$$
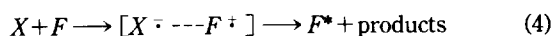
The ϕ_{ex} of 1-aminoanthracene was enhanced since both radical ions are possibly stabilized in the polar region of the surfactants and thus the recombination that results in the excited state is apparently enhanced. The radical anion is assumed to be polar albeit its structure is still in controversy. On the other hand, the radical cation of anthracene, due to its hydrophobicity, is apparently migrated and located in the nonpolar region of the surfactants. Thus the separation between radical ions becomes so large that the excitation is interfered. In is not uncommon that radical species are stabilized in a micellar medium. Nitrobenzene radical anion, *e.g.*, is stabilized in SDS micelle when Li^+ is present.[13] Furthermore, Birks and coworkers reported earlier that the stability of the charge transfer complex or radical cation produced from electron transfer may be greater for amino-PAH than other fluorescers.[3b]

When [surfactant] becomes too high, however, I_{CL} shows a decrease. Since I_f was not varied at such high [surfactant] it appears that the reaction between X and F was probably interfered with large concentration of surfactant. At the present it is not certain which species are involved in the competing reaction that reduces I_{CL} and which species are more stabilized in the presence of surfactant. Further studies are underway to elucidate the complex nature of the energy transfer. Nevertheless, it is highly desirable from analytical viewpoint that the sensitivity of amino-PAH detection can be improved by using surfactants over other fluorescers.

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Catalytic Effects of Anion-Exchange Resins on the Methylation of 2-Methoxyphenolate Anion

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Synthetic polymers have been employed as catalysts for many organic reactions. The catalysis may arise from the increase in the effective concentrations of reactants on the surface of the polymer,[1] changes in the pH of the microenvironment on the polymer,[2] or the increased hydrophobicity of the polymer domain.[2] Ion-exchange resins catalyze some organic reactions by acting as heterogeneous sources of acids and bases.[3]

Alkylation of the carbanion derived from ethyl 2-ethylacetoacetate with ethyl bromide is catalyzed by anion-exchange resins.[4] The anion-exchange resins contain quaternary ammonium ions. When the carbanion is adsorbed on the polymer surface, the effective size of the counter-cation is increased. Due to the reduced electrostatic interaction with the counter-cation, the carbanion becomes more naked, resulting in the increase in the intrinsic reactivity. In addition, the naked carbanion of the 2-ethylacetoacetate ester appears to be partially relieved of the steric crowdedness, leading to further rate enhancement.

Addition of crown ethers also catalyzed the ethylation of the carbanion derived from ethyl 2-ethylacetoacetate.[5] This is also attributable to the increase in the effective size of the counter-cation. Whether the reduced electrostatic interaction of the counter-cation with the anionic reactant results in the rate-enhancement or rate-retardation, however, depends on the type of the reaction.[6] If the transition state possesses smaller density of negative charge compared with the ground state, the reaction would be accelerated considerably by reducing the electrostatic interaction.

In the present study, the catalytic effects of the anion-exchange resins is extended to the reaction of 2-methoxyphenolate with methyl iodide. Unlike the alkylation of the carbanion of ethyl 2-ethylacetoacetate, this reaction does not in-

Table 1. Yield of Methylation of Sodium 2-Methoxyphenolate in the Presence of Various Types of Anion-Exchange Resins[a]

Dowex resin		Yield (%)
Type	Active group[b]	
no resin added		30 [17][c] (26)[d]
1×1-100	I	19
1×2-100	I	25
1×4-50	I	28
1×8-50	I	24
2×8-50	II	37 [28][c] (23)[d]
WGR-2	III	0.5 (0.5)[d]
SBR	IV	95 [80][c] (87)[d]
SBR-P	IV[e]	87 [60][c]

[a]Unless noted otherwise, methylation was carried out for 4 days in 33 % (v/v) ethanol-water (15 m*l*) with 0.20 g sodium 2-methoxyphenolate, 0.30 m*l* methyl iodide (3.5 equivalent), and 1.0 g resin at room temperature, and the mixture was constantly stirred with a magnetic stirring bar. [b]I: Ph-CH$_2$-N(CH$_3$)$_3$$^+Cl^-$, II: Ph-CH$_2$-N(CH$_3$)$_2$(CH$_2CH_2$OH)$^+Cl^-$, III: Ph-CH$_2$-N(CH$_3$)$_2H^+Cl^-$, IV: Ph-CH$_2$-N(CH$_3$)$_3$$^+OH^-$. [c]Reaction mixture was not stirred during the incubation period. [d]Dimethyl sulfate (0.30 m*l*, 2.3 equivalent) was used instead of methyl iodide. [e]Porous.

volve significant steric hindrance. Thus, the methylation of 2-methoxyphenolate is a typical S$_N$2 reaction between an anionic nucleophile and a neutral molecule without complications from steric aspects. This type of S$_N$2 reaction is accompanied by the dispersion of the negative charge in the transition state and is known to be greatly accelerated in dipolar aprotic solvents.[7]

$$CH_3X + NaO\text{-}C_6H_4\text{-}2\text{-}OCH_3 \longrightarrow 1,2\text{-}(CH_3O)_2C_6H_4 + NaX \quad (1)$$
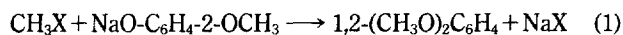
A Dowex anion-exchange resin purchased from Sigma Chemical Co. was swollen for 1 hr in the reaction medium. To the stirred mixture was added sodium 2-methoxyphenolate and, 10 min later, methyl iodide or dimethyl sulfate to initiate the methylation reaction. The methylation was carried out under an atmosphere of nitrogen. Progress of the methylation was measured by gas chromatography.

Yields of the methylation reaction carried out in the absence or presence of various types of anion-exchange resins are summarized in Table 1. The yields reached plateau values within 4 days of incubation. The period of time needed for accomplishing the maximum yield was generally shorter when the maximum yield was greater.

As indicated in Table 1, resins SBR and SBR-P exert considerable catalytic effects and resin WGR-2 remarkably inhibits the methylation reaction, whereas the remaining resins do not manifest appreciable effects. The inhibitory action of resin WGR-2 can be ascribed to the protonation of 2-methoxyphenolate anion by the hydrogen chloride portion bound to the resin.

In Figure 1, yield of the methylation is plotted against the amount of resin SBR-P. The saturation behavior manifested in the figure is consistent with the adsorption of the reactants to the polymer surface and the reaction between the adsorbed reactants. Then, the lack of catalytic effect of
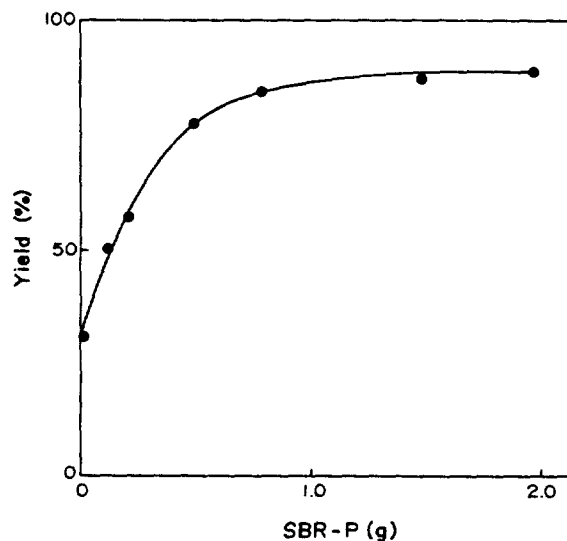
Figure 1. Yield of methylation of sodium 2-methoxyphenolate with methyl iodide plotted against amount of resin SBR-P added as the catalyst. For reaction conditions, see footnote a of Table 1.

the resins containing the chloride counter-anion can be explained in terms of the inhibition by chloride ion. Since chloride ion has greater affinity to the anion exchange resins compared with hydroxide ion, the adsorption of the 2-methoxyphenolate anion to the polymer surface would be inhibited much more effectively by the chloride counter-anion.

In the previously investigated catalysis by anion-exchange resins in the ethylation of the carbanion of ethyl 2-ethylacetoacetate, resin SBR is much more effective than the resins with chloride counter-anions. This is also attributed to easier adsorption of the anionic reactant to the polymer surface when hydroxide instead of chloride is the counter-anion.

The effective catalysis by resins SBR and SBR-P indicates that the S$_N$2 reaction between the 2-methoxyphenolate anion and the methylating agent proceeds more readily on the polymer surface than in the bulk medium. This type of S$_N$2 reactions is greatly accelerated in dipolar aprotic solvents, and the acceleration arises from the lack of stabilization of the anionic center by solvation.[8] Similarly, the electrostatic stabilization of the anionic reactant would be reduced upon adsorption to the surface of the anion-exchange resins, leading to the observed catalytic effects.

The difference in the effective pH of the microdomain on the polymer may also affect the yield of the methylating reaction. Greater effective pH of the microdomain would facilitate both the ionization of 2-methoxyphenol and the destruction of the alkylating agent. Under the experimental conditions, the soium salt of 2-methoxyphenolate is employed, and, thus, the effect of the effective pH on the ionization of 2-methoxyphenol is not important when the resin contains quaternary ammonium ions. Among the anion-exchange resins, the effective pH of SBR or SBR-P would be higher than those of the other polymers since SBR or SBR-P contains hydroxide ion as the counterion. In addition, the alkylating agents would be adsorbed more readily to the more hydrophobic polymers. Then, the destruction of alkylating agents by the attack of hydroxide ion or ethoxide ion would be faster in the micro-

domain of SBR or SBR-P than in those of other resins. The higher effective pH in the microdomain of SBR or SBR-P, therefore, does not appear to be directly related to the enhanced yield of the methylation reaction in the presence of these resins.

Alkylation of phenolate anions is involved in the preparation of many pharmaceuticals. The anion-exchange resins are cheap, and separation of the catalyst from the products is very simple when the resins are used. Thus, ion-exchange resins may have wide applications in various synthetic reactions, especially on industrial scales.

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Oxidation of Alcohols with NiO₂-Al₂O₃

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Selective oxidation of allylic and benzylic hydroxy groups in the presence of aliphatic hydroxy groups is a useful transformation in organic synthesis. Although there are several reagents available for this purpose, these oxidizing agents do not show sufficient selectivity, or are not generally applicable, or are not readilly available. For example, the widely used manganese dioxide oxidizes aliphatic alcohols in certain cases.[1] Even chromium (VI) reagents such as bis(tetrabutyl-ammonium)dichromate[2] and 4-dimethylaminopyridinium chlorochromate,[3] which have recently reported and were

Table 1. Oxidation of Benzylic and Allylic Alcohols with NiO₂-Al₂O₃ in Benzene

Alcohols	Products	Time, h	Yield, %[a,b]
benzyl alcohol	benzaldehyde	3	98
sec-phenethyl alcohol	acetophenone	3	97
p-anisyl alcohol	*p*-anisaldehyde	5	(85)
benzhydrol	benzophenone	2	(95)
allyl alcohol	acrolein	3	98
3-buten-2-ol	3-buten-2-one	2	98
crotyl alcohol	crotonaldehyde	3	99
cinnamyl acohol	cinnamaldehvde	3	98
geraniol	geranial	6	85
1	2	2	(90)

[a] The yields were determined by GC. [b] The yields in parentheses are isolated ones.
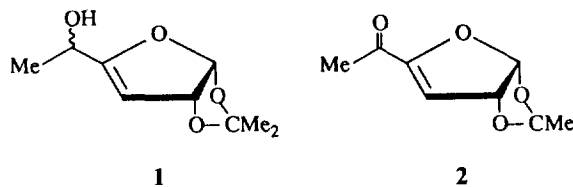
claimed to be superior to other selective oxidizing agents, still oxidize saturated primary and secondary alcohols to a significant extent. We have also reported that potassium ferrate,[4] potassium ruthenate,[5] and potassium manganate[6] under phase-transfer catalysis conditions selectively oxidizes allylic and benzylic alcohols. Although nickel peroxide, NiO₂, has been known as an oxidizing agent for a long time[7] and has been used for the oxidation of alcohols,[8] its utility has been limited in organic synthesis because it has not shown advantages over versatile manganese dioxide, MnO₂. Another reason for the limited utility of nickel peroxide is its insolubility in organic solvents. This problem, however, can be overcome by employing heterogeneous reactions on solid supports. In this communication, we report that a solid mixture of nickel peroxide[9] and Woelm 200 basic chromatographic alumina[10] is a more efficient and selective oxidizing system for allylic and benzylic alcohols than the most widely used manganese dioxide. We have also found that NiO₂-Al₂O₃ system cleaves vicinal diols.

The oxidation on the solid support in the present work was performed by stirring the benzene solution (10 m*l*) of an alcohol (1.00 mmol) with the solid mixture[11] of nickel peroxide (0.46 g, 1.50 mmol) and Al₂O₃ (W-200-B) (0.46 g) at room temperature under nitrogen. After completion of the reaction, the solid reagent was removed by the filtration and evaporation of the solvent afforded the product. Benzyl alcohol was readily oxidized to benzaldehyde by this solid oxidizing agent in 2 h in 98% yield. Other benzylic alcohols were similarly transformed into the corresponding aldehydes or ketones in high yields as shown in Table 1. NiO₂-Al₂O₃ system was also effective for the oxidation of allylic alcohols to the corresponding α, β-unsaturated aldehydes or ketones. On the other hand, aliphatic primary and secondary alcohols such as 1-decanol, 1-dodecanol, 4-phenylcyclohexanol, and 2-heptanol were not oxidized by NiO₂-Al₂O₃ in prolonged reaction time at higher reaction temperature. Table 1 clearly