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Control of the Selectivity and Increase of the Catalytic Activity of Polynaphthoquinone by Various Lewis Acids

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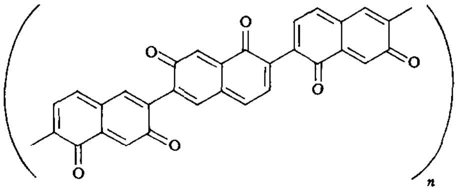
A control of the reactivity and an increase of the catalytic activity of polynaphthoquinones containing various Lewis acids, i.e., $MoCl_5$, VCl_3, $FeCl_3$, $ZnCl_2$ and $CuCl_2$, are reported. The polynaphthoquinone containing Lewis acids is considered to be a typical heterogeneous catalyst which has both acid and basic sites; Lewis acids added act as acid sites, while quinone groups in the polymer correspond to basic sites. As model reactions the decompositions of ethyl and isopropyl alcohols were studied in the temperature range from 150 to 210°C. Langmuir type adsorption of ethyl alcohol on these catalysts was confirmed. Lewis acids added to the polynaphthoquinone acted as adsorption sites as well as active sites of the reaction. The selectivity of the reaction on the polynaphthoquinone containing Lewis acids was markedly affected by the alcohols used. The selectivity of the decomposition of the alcohols is conveniently controlled by both modifying the polynaphthoquinone and adding different natures of Lewis acids.

Both an increase of the catalytic activity and a control of the reactivity of catalysts are major problems in catalytic chemistry as well as important subjects to be solved in connection with enzymic reaction in biochemistry. Quinone compounds play a characteristic role in living bodies, functioning, in many cases, as hydrogen or electron carriers (*1*). The organic polymers containing quinone groups (*2*) are considered to have relatively well-defined surface with uniformly distributed active sites. The quinone polymers with Lewis acids are also regarded as heterogeneous catalytic systems having both acid and basic sites. It is accordingly interesting to investigate the control of the selectivity and the catalytic activity of such catalysts with the quinone groups coordinated with various natures of metal halides.

Polynaphthoquinone containing quinone groups has been found to act as a highly active catalyst for many reactions (*3*). The selectivity of the decomposition of ethyl alcohol over the polynaphthoquinones having various amounts of $FeCl_3$ was previously reported (*4*). In the present paper the study on the control of the selectivity of the decomposition of ethyl and isopropyl alcohols on the polynaphthoquinones containing various Lewis acids (i.e., $MoCl_5$, VCl_3, $FeCl_2$, $ZnCl_2$ and $CuCl_2$) is reported.

EXPERIMENTAL METHODS

Polynaphthoquinone employed as the metal-free catalyst in this study was obtained by the oxidation of 1,7-naphthalenediol with aqueous 14% nitric acid in a similar procedure to that described previously except for slight modifications (*3*). Polynaphthoquinone was heated at 340°C for 6 hr under vacuum. The polynaphthoquinone:



is a planar molecule and the planar polymers are tightly aggregated to form the porous insoluble polynaphthoquinone catalyst (ca. 70 m^2/g) (*5*). The polynaphthoquinones containing various Lewis acids ($MoCl_5$, VCl_3, $FeCl_3$, $ZnCl_2$ and $CuCl_2$) were prepared by mixing 0.1 g of the polynaphthoquinone and known amounts of Lewis acids in ethyl alcohol, or diethyl ether in the absence of air, followed by slow evaporation of the solvent at the room temperature in vacuum. The Lewis acid-containing polynaphthoquinones thus obtained were treated at 340°C for 12 hr under vacuum before use as a catalyst.

All of chemicals used were of CP grade. Ethyl and isopropyl alcohols were further purified by distillation after removal of water by molecular sieves under dry nitrogen.

The decompositions of ethyl and isopropyl alcohols were always carried out in a closed circulating system (162 cm^3) using the catalyst having 0.1 g of the polynaphthoquinone. Prior to each run, air (30 cm Hg) was introduced to the system and circulated through the catalyst at 210°C for 30 min, followed by treating at 340°C for 1 hr under vacuum. The reaction products were quantitatively analyzed by gas chromatography, using a dioctyl sebacate column at 80°C. The amounts of ethyl alcohol adsorbed on the catalysts were volumetrically determined, taking the adsorption of the vapor by the apparatus into consideration.

The ir spectra of the coordinated complexes of various Lewis acids with α-, or β-naphthoquinone were measured by means of a usual KBr disk method; naphthoquinones were chosen as the model compounds containing a quinone group. The naphthoquinone complexes with Lewis acids were obtained as the precipitates from a mixture of α- or β-naphthoquinone and a Lewis acid in ethyl alcohol, acetone or chloroform, followed by slow removal of the solvent. The coordinated complexes of xanthone with Lewis acids were also prepared from their concentrated solutions by gradually evaporating the solvent as was reported by Cook (*6*).

RESULTS AND DISCUSSION

Adsorption of Ethyl Alcohol on the Polynaphthoquinones Containing Various Lewis Acids

The adsorptions of ethyl alcohol on the Lewis acid-containing polynaphthoquinones and on the metal-free polynaphthoquinone were measured by manometry in the temperature range from 150 to 210°C. Adsorption is rapid and completely within 11 min. The adsorption was found to be expressed by the Langmuir equation as was previously described (*4*), $V_{ad} = bKP/(1 + KP)$, where V_{ad} is the volume adsorbed and b and K are the saturation mass adsorbed and the equilibrium constant for the adsorption, respectively. The results on the polynaphthoquinones containing various kinds of Lewis acids at 190°C are given in Fig. 1. The saturation mass adsorbed remains unchanged at different temperatures. The heats of adsorptions on the polynaphthoquinones containing 7 mol% of $CuCl_2$, $ZnCl_2$, $FeCl_3$, VCl_3 and $MoCl_5$, were found to be 8.7,

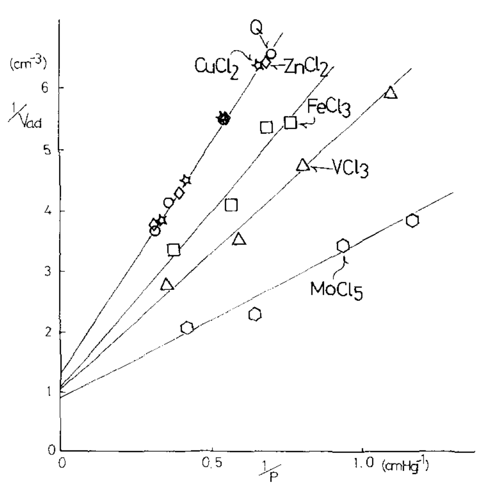


FIG. 1. Langmuir plots of the ethyl alcohol adsorption on the polynaphthoquinone (0.1 g) containing 7 mol% of Lewis acids at 190°C.

8.9, 7.5, 7.5 and 7.2 kcal/mol, respectively, while that on the metal-free polynaphthoquinone was 8.7 kcal/mol. These values correspond to the energy of a hydrogen bond. Although the values decreased by the addition of the Lewis acids to the polynaphthoquinone, the equilibrium constant for the adsorption increased by the Lewis acid addition because of an increase of the entropy parts in the thermodynamical parameters for the adsorption. The saturation mass adsorbed was influenced by the nature of Lewis acids added; Q, 7.4 cm^3 (STP)/cat-g; Q-$CuCl_2$, 6.9; Q-$ZnCl_2$, 7.2; Q-$FeCl_3$, 9.0; Q-VCl_3, 9.3; and Q-$MoCl_5$, 11.0, where Q stands for the polynaphthoquinone. The adsorbed amounts of ethyl alcohol on the Lewis acid-containing polynaphthoquinone were, consequently, found to increase in the following order of added Lewis acids: metal-free $\sim$ $CuCl_2$ $\sim$ $ZnCl_2$ $<$ $FeCl_3$ $<$ VCl_3 $<$ $MoCl_5$. The amount of adsorption increased with the Lewis acid content of the catalyst. The saturation mass adsorbed was proportional to the amount of the Lewis acid contained in the catalyst as shown in Fig. 2. These results indicate that the Lewis acids in the polymer work as adsorption sites; $MoCl_5$ was most effective in the Lewis acids added to the polynaphthoquinone for providing adsorption sites.

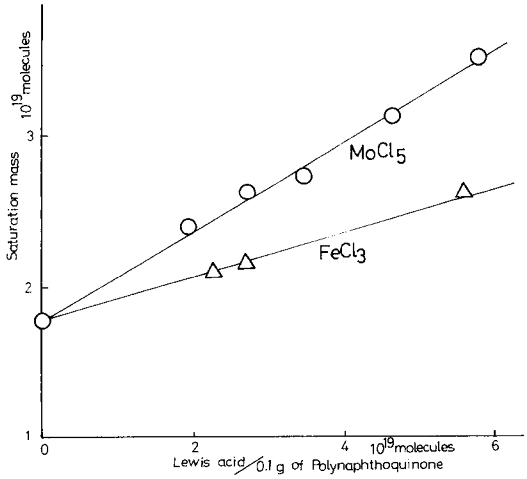


FIG. 2. Dependence of the saturation mass adsorbed of ethyl alcohol upon the $MoCl_5$ and $FeCl_3$ content.

Processes of the Dehydrogenation and the Dehydration of Alcohols

The decomposition of ethyl alcohol to acetaldehyde, ethylene and diethyl ether over the polynaphthoquinones with or without Lewis acids was studied in the temperature range from 150 to 210°C in the absence of oxygen in a closed circulating system (162 cm^3). The decomposition of diethyl ether to form ethylene was negligible under a similar condition. The reaction was slightly inhibited by the reaction products. Accordingly, the initial stage of the reaction was investigated to obtain the information on the activation of the polynaphthoquinone by the addition of Lewis acids and on the control of the selectivity by Lewis acids added.

The dehydrogenation of ethyl alcohol rapidly proceeded to produce acetaldehyde on the polynaphthoquinones containing various Lewis acids (i.e., $CuCl_2$, $ZnCl_2$, $FeCl_3$, VCl_3 and $MoCl_5$) in the temperature range from 150 to 210°C. The initial rate of the formation of acetaldehyde on the catalysts was proportional to the amount of ethyl alcohol adsorbed on the catalysts. Figure 3 is the result at 200°C on the polynaphthoquinone containing 7 mol% of VCl_3. Accordingly, the rate equation is expressed as follows; $d(\text{acetaldehyde})/dt = k_1\,(\text{ethyl alcohol})_{ad}$, where $(\text{ethyl alcohol})_{ad}$ represents the amount of ethyl alcohol adsorbed on the surface of the polynaphthoquinone. This is also equal to be $k_1bKP/(1+KP)$. Consequently, acetaldehyde is formed by a surface unimolecular process of ethyl alcohol on the catalyst, where a surface reaction involving the adsorbed ethyl alcohol is the rate-determining step.

The formation of acetaldehyde was remarkably enhanced by adding Lewis acids to the polynaphthoquinone. The initial rate of the dehydrogenation depended upon the

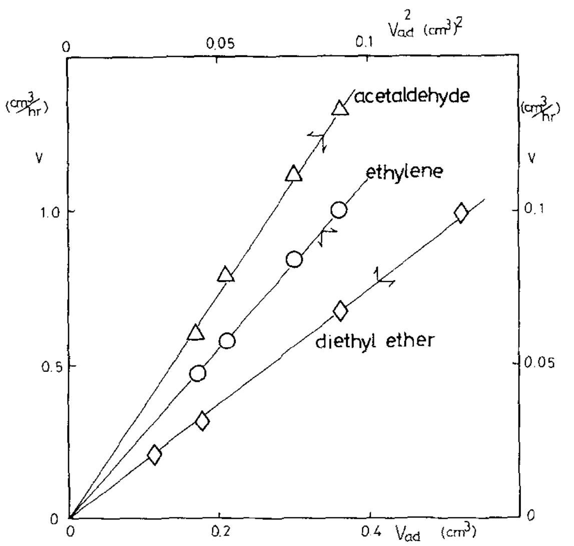
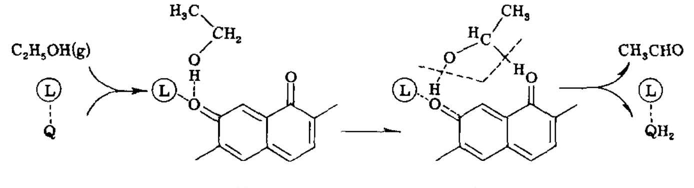


FIG. 3. Dependence of initial rates (v) of the formation of acetaldehyde, ethylene and diethyl ether upon adsorbed amounts (V_{ad}) of ethyl alcohol over the polynaphthoquinone (0.1 g) containing 7 mol% of VCl_3 at 200°C.

nature of the Lewis acid added as is given in Table 1. The initial rate of the dehydrogenation is plotted against the amount of $MoCl_5$ contained in the polynaphthoquinone in Fig. 4, where the initial rates increased linearly with the $MoCl_5$ content. The rate per active site which were estimated from the $MoCl_5$ content, were independent of the amount of $MoCl_5$. These results indicate that all of the Lewis acids added to the polymer behave uniformly as active sites for the overall reaction as well as for adsorption.

Thus the dehydrogenation of ethyl alcohol over the polynaphthoquinones containing various Lewis acids is shown in a similar scheme to that described previously (*4*) as follows:



(I) (II)

where L and QH_2 represent Lewis acids coordinating to the quinone group and the reduced polynaphthoquinone containing hydroquinone groups, respectively. The adsorption of ethyl alcohol on the Lewis acid-containing polynaphthoquinone is represented by (I). The process shows that the quinone groups activated by Lewis acids work as active sites in the dehydrogenation of ethyl alcohol. The Lewis acid added to the polynaphthoquinone enhances the dehydrogenative activity of the quinone group in the catalyst.

The reaction proceeds until the polynaphthoquinone surface is saturated with hydrogen. No hydrogen is evolved during the dehydrogenation process, a characteristic property of quinone polymers. The dehydrogenation on the polynaphthoquinones is recognized to be hydrogen transfer from the substrate to the quinone group of the polymer. This is another dis-

TABLE 1

THE FORMATION OF ACETALDEHYDE (A), ETHYLENE (E) AND DIETHYL ETHER (DE) FROM ETHYL ALCOHOL (2 cm Hg) OVER THE POLYNAPHTHOQUINONE CONTAINING 7 mol% OF LEWIS ACIDS AT 200°C

Catalyst[a]	Initial rate[b] (cm^3/hr)			Relative rate			Rate constant[c]			Activation energy (kcal/mol)		
	A	E	DE	A	E	DE	A	E	DE	A	E	DE
Q	0.080	0.014	0.004	1	1	1	0.44	0.080	0.13	23.0	26.2	30.1
Q-$CuCl_2$	0.14	0.016	0.005	1.8	1.1	1.2	0.76	0.086	0.14	22.0	26.6	29.4
Q-$ZnCl_2$	0.16	0.019	0.006	2.0	1.3	1.5	0.83	0.10	0.17	22.0	26.0	29.2
Q-$FeCl_3$	0.80	0.064	0.032	10.0	4.5	7.8	3.20	0.26	0.51	16.3	20.0	23.0
Q-VCl_3	1.11	0.084	0.067	13.9	5.8	16.5	3.70	0.28	0.75	15.1	20.0	21.9
Q-$MoCl_5$	2.80	0.22	0.45	35.0	15.3	109.8	6.09	0.44	2.13	12.7	18.0	18.0

[a] Q: polynaphthoquinone (0.1 g).

[b] $v = k_1$(ethyl alcohol)$_{ad}$ for the formation of A, $v = k_2$(ethyl alcohol)$_{ad}$ for the formation of E and $v = k_3$(ethyl alcohol)$_{ad}^2$ for the formation of DE.

[c] $k_1(hr^{-1})$ for A, $k_2(hr^{-1})$ for E and $k_3(cm^{-3}\ hr^{-1})$ for DE.

tinguished property of organic polymers containing quinone groups which have relatively well-defined active sites. When oxygen is admitted onto the reduced polynaphthoquinone containing hydroquinone groups, these groups are easily reoxidized to regenerate quinones accompanied with the formation of water via hydrogen peroxide as was reported in the previous paper (*4*). Accordingly, the dehydrogenation of ethyl alcohol on the polynaphthoquinones catalytically proceeds in the presence of oxygen.

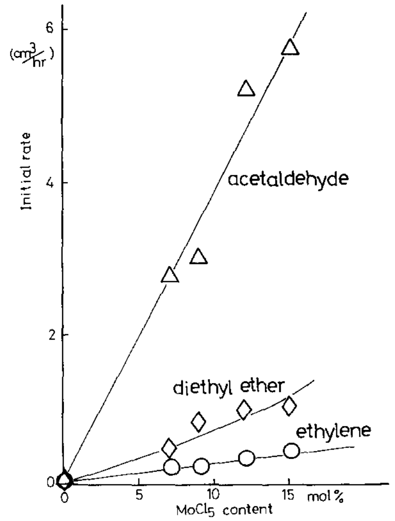


FIG. 4. Relation of initial rates of the formations of acetaldehyde, ethylene and diethyl ether with the $MoCl_5$ content of 0.1 g of the polynaphthoquinone at 200°C.

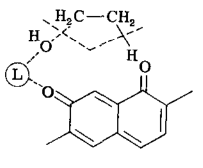
The dehydration of ethyl alcohol on the Lewis acid-containing polynaphthoquinones also took place in the temperature range from 150 to 210°C. The initial rates of the formation of ethylene and diethyl ether are plotted against the amount of ethyl alcohol adsorbed on the catalyst in Fig. 3; the rate of the ethylene formation was proportional to the adsorbed amount of ethyl alcohol, while the initial rate of the diethyl ether formation had a good correlation with the square of the adsorbed amount of ethyl alcohol. Accordingly, the initial rates of the formations of ethylene and diethyl ether, respectively, obey the following equations:

$$d(\text{ethylene})/dt = k_2(\text{ethyl alcohol})_{ad} = k_2bKP/(1 + KP), \text{ and}$$
$$d(\text{diethyl ether})/dt = k_3(\text{ethyl alcohol})_{ad}^2 = k_3b^2K^2P^2/(1 + KP)^2.$$

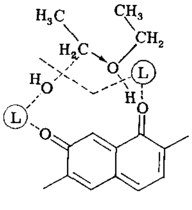
Consequently, ethylene and diethyl ether are formed by unimolecular reaction of the adsorbed ethyl alcohol and by a surface bimolecular reaction between ethyl alcohol molecules adsorbed on the catalyst, respectively.

The relations of the initial rates of the formation of ethylene and diethyl ether with the Lewis acid content of the polynaphthoquinone are shown in Fig. 4. The initial rates of the ethylene formation increased linearly with the amount of $MoCl_5$ added. As was previously observed on the $FeCl_3$-containing polynaphthoquinone, the formation of diethyl ether on the polynaphthoquinone containing $MoCl_5$ also seems to have a correlation with the square of the Lewis acid content, though its relation in the small content of Lewis acid was almost linear.

Consequently, the dehydration of ethyl alcohol on the polynaphthoquinone containing various Lewis acids is expressed by the same scheme as that described previously.



(III)



(IV)

(III) shows the transition state of the ethylene formation, in which the hydroxyl anion is removed from ethyl alcohol by the Lewis acid, accompanied with removal of a proton by the quinone group. Thus ethylene is produced. Diethyl ether is formed from two ethyl alcohol molecules adsorbed on the catalyst surface through (IV); the ethyl carbonium ion produced by removal of the hydroxyl anion by the Lewis acid electrophilically attacks the oxygen atom of an adjacent ethyl alcohol molecule, while a proton is removed by the quinone group activated by Lewis acid.

The decomposition of isopropyl alcohol to form acetone and propylene was also studied on the polynaphthoquinones containing Lewis acids like $MoCl_5$, VCl_3, $FeCl_3$, $ZnCl_2$ and $CuCl_2$. The results at 170°C are given in Table 2. The initial rates of the dehydrogenation and dehydration of isopropyl alcohol were markedly influenced by the nature of added Lewis acids. The relations of the initial rates of the formations of acetone and propylene with the $MoCl_5$ content of the polynaphthoquinone are shown in Fig. 5, where both rates varied in proportion to the $MoCl_5$ content. Accordingly, the decomposition of isopropyl alcohol on the Lewis acid-containing catalyst is expressed by the same scheme as that of ethyl alcohol.

TABLE 2

THE FORMATION OF ACETONE (AC) AND PROPYLENE (PR) FROM ISOPROPYL ALCOHOL ON THE POLYNAPHTHOQUINONE CONTAINING 7 mol% OF LEWIS ACIDS AT 170°C[a]

Catalyst	Initial rate (cm^3/hr) Ac	Initial rate (cm^3/hr) Pr	Relative rate Ac	Relative rate Pr
Q	0.097	0.028	1	1
Q-$CuCl_2$	0.19	0.086	1.9	3.0
Q-$ZnCl_2$	0.18	0.21	1.9	7.3
Q-$FeCl_3$	0.22	0.44	2.3	15.5
Q-VCl_3	0.53	1.82	5.5	64.3
Q-$MoCl_5$	1.43	9.54	14.8	337.1

[a] Initial pressure of isopropyl alcohol = 2.0 cm Hg.

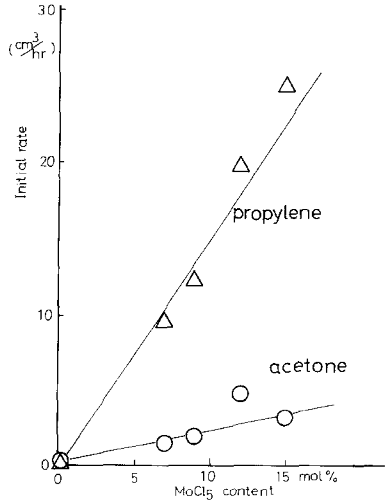


FIG. 5. Relation of initial rates of the formations of propylene and acetone with the $MoCl_5$ content of 0.1 g of the polynaphthoquinone at 170°C.

However, the formation of diisopropyl ether was negligible under these conditions.

Control of the Reactivity of the Polynaphthoquinone

As was previously reported (*3*), $FeCl_3$ forms the coordinated complex with violanthrone chosen as a model compound having a quinone group. In the present study α- or β-naphthoquinone was employed as a model compound and the ir spectra of their complexes with various Lewis acids were measured by means of KBr disk method. The ir absorption peak of the quinone group of α- or β-naphthoquinone was perturbed by adding Lewis acids to the naphthoquinones in ethyl alcohol, chloroform, or acetone. These results indicate that the polynaphthoquinone forms coordinated complexes with Lewis acids, via the quinone groups.

Cook demonstrated (*6*) that the shift of the carbonyl stretching virbration in xanthone molecule coordinated by Lewis acids was related to the strength of the interaction between the basic oxygen atom and the Lewis acid. The amount of the shift of the quinone absorption peak of α- or β-naphthoquinone by the addition of Lewis acids was not accurately determined, but the perturbation of the quinone stretching frequency seemed to be associated with the Lewis acid strength. Accordingly, the shift of the carbonyl stretching frequency of xanthone molecule in xanthone–Lewis acids complexes (*7*) was used as an estimate of the strength of the acidity of Lewis acids. The shift of the absorption peak towards lower frequencies implies that the strength of the C═O double bond decreased. The logarithms of the rate constants of the dehydrogenation on the Lewis acid-containing polynaphthoquinones had a nearly parallel relation with the perturbation of the C═O stretching frequency on the addition of Lewis acids. These results indicate that the decrease of the energy of the quinone bond caused by the coordination of Lewis acids results in the decrease of the activation energy of the reaction. Consequently, the interaction between added Lewis acid and the quinone group in the polynaphthoquinone may contribute to weakening the quinone linkage; accordingly, quinone groups (C═O double bond) are easily converted to hydroquinone groups (C—O single bond). Thus the stronger Lewis acid added more markedly enhances the dehydrogenative activity of the polynaphthoquinone.

The relative rates against the rate on the metal-free polynaphthoquinone (Q) are given in Table 1. It was consequently found that the decomposition of ethyl alcohol was accelerated by a factor of 15- 110 by adding $MoCl_5$ to the catalyst.

The selectivity of the formation of acetaldehyde and ethylene may be decided by the relative rates of the two reactions; one reaction proceeds via (II) in the scheme and another by way of (III). The dehydrogenation of ethyl alcohol through (II) takes place more easily than dehydration through (III) over the catalyst containing Lewis acids. The dehydrogenation of ethyl alcohol over the Lewis acid-containing polynaphthoquinones accounts for about 90% of the reaction at 150°C and for about 84% at 200°C, the value being almost independent of the kind of added Lewis acids. Ethyl alcohol on the polynaphthoquinone is mainly dehydrogenated to catalytically form acetaldehyde in the presence of oxygen. This shows that the polynaphthoquinones containing Lewis acids work as active catalysts for the dehydrogenation of ethyl alcohol in the presence of oxygen or air.

The dehydrogenation in the absence of oxygen stops when the active quinone groups in the polymer have been reduced as was previously described. However, the dehydration to form ethylene on the catalysts with Lewis acids except for the $MoCl_5$-containing catalyst, is much less influenced by the reduction of the quinone groups; the rate of the dehydration on the $MoCl_5$-containing polynaphthoquinone somewhat decreases by it. Consequently, ethylene rather than acetaldehyde is predominantly produced over the reduced polynaphthoquinone, thus altering the selectivity of the reaction by modifying the catalysts.

When isopropyl alcohol was used as a substrate, isopropyl alcohol was decomposed to acetone and propylene on the polynaphthoquinones containing Lewis acids. Negligible diisopropyl ether was observed. Lewis acids added enhanced the formation of propylene much more than that of acetone as is shown in the relative rates of Table 2. Isopropyl alcohol on the metal-free polynaphthoquinone and on the $CuCl_2$-containing polynaphthoquinone is mainly dehydrogenated to form acetone. However, on the polynaphthoquinones containing Lewis acids like $FeCl_3$, VCl_3 and $MoCl_5$, propylene is predominantly produced even in the presence of oxygen. The selectivity of the reaction on the polynaphthoquinones containing various Lewis acids was markedly affected by the alcohols used. The selectivity of the decomposition of isopropyl alcohol at 170°C is plotted against the perturbation of the C=O stretching frequency (*7*) in the xanthone-Lewis acid complexes in Fig. 6, where the perturbation was regarded as an estimate of the acid strength of the Lewis acids contained in the polynaphthoquinone. It was noted that the selectivity of the reaction markedly depended upon the nature of Lewis acids added. Accordingly, the selectivity of the reaction on the polynaphthoquinones is conveniently controlled by adding different natures of Lewis acids to the polynaphthoquinone.

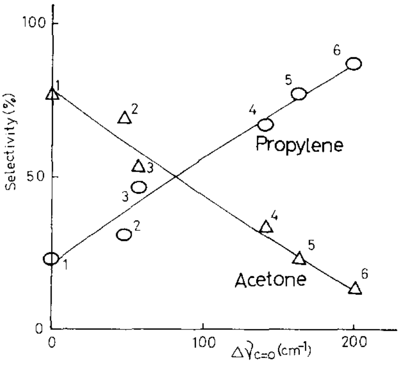


FIG. 6. Dependence of the selectivity of the dehydrogenation and the dehydration of isopropyl alcohol over the Lewis acid-containing polynaphthoquinones upon the nature of Lewis acids (the perturbation of the C=O stretching frequency) (*7*) at 170°C: (1) the metal-free polynaphthoquinone (Q), (2) Q-$CuCl_2$, (3) Q-$ZnCl_2$, (4) Q-$FeCl_3$, (5) Q-VCL_3, (6) Q-$MoCl_5$, Lewis acid content = 7 mol%, initial pressure of alcohol = 2.0 cm Hg.

As shown in (IV), two molecules of ethyl alcohol are required to adsorb close together for the formation of diethyl ether. The electrophilic attack of the ethyl carbonium ion to the oxygen atom of an adjacent ethyl alcohol molecules is the rate-determining step in the formation of diethyl ether; the ethyl carbonium ion is produced by removal of the hydroxyl anion by the Lewis acid. The rate of the attack of the ethyl carbonium ion to the oxygen atom may be accelerated by a pull of a proton from the hydroxyl group of an adjacent ethyl alcohol by the quinone group of the polynaphthoquinone [see (IV)]. The pull of a proton from the hydroxyl group results in an increase of the electron density on the oxygen atom of an adjacent ethyl alcohol; such electron sufficiency favors the electrophilic attack by the ethyl carbonium ion. Accordingly, the formation of diethyl ether is recognized to be a combined action of the Lewis acid added to the polynaphthoquinone and the quinone group activated by the Lewis acid as shown in (IV).

It is understood on metal oxide catalysts (*8*) that ethers formed from alcohols are produced from two molecules of alcohol, one adsorbing on an acid site of the catalyst and another on a basic site. The polynaphthoquinones containing Lewis acids behave as typical heterogeneous acid–base catalysts. The Lewis acid added to the catalyst acts as an acid site and the quinone group corresponds to the basic site. The organic polymers containing quinone groups are considered to have uniformly distributed active sites and a relatively well-defined surface.

The initial rates and the rate constants of the formations of ethylene and diethyl ether on the polynaphthoquinones containing various Lewis acids at 200°C are given in Table 1, where the activation energies of the reactions are also given. The rate constants were increased by adding the Lewis acids having the stronger acidity. The rate constant for the formation of diethyl ether was found to be more influenced by the addition of Lewis acids to the catalyst than that for the ethylene formation. Diethyl ether is formed by a bimolecular process between two ethyl alcohol molecules closely adsorbed through (IV), while ethylene is produced by a unimolecular reaction through (III). The greater the amount of ethyl alcohol adsorbed, the higher the ratio of diethyl ether formed to that of ethylene. Accordingly, the initial rate of the formation of diethyl ether rather than that of ethylene was markedly affected by the nature of Lewis acids added to the polynaphthoquinone (see the relative rates in Table 1).

The selectivity between the formations of diethyl ether and ethylene are plotted against the shift of the C═O stretching frequency (7) in the xanthone–Lewis acid complexes in Fig. 7, where the shift was used as an estimate of the strength of the acidity of added Lewis acids. Ethylene is predominantly produced on the polynaphthoquinones containing $CuCl_2$, $ZnCl_2$ and $FeCl_3$, and on the VCl_3-containing catalyst the ethylene formation accounts for 55% of the dehydration reaction, whereas the formation of diethyl ether predominates on the polynaphthoquinone containing $MoCl_5$. The ratio of the initial rate of the diethyl ether formation to that of the ethylene formation was also found to increase with an increase of the initial pressure of ethyl alcohol and the amount of Lewis acids added.

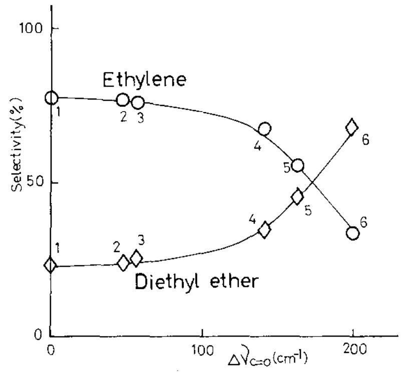


FIG. 7. Dependence of the selectivity of the formation of ethylene and diethyl ether over the Lewis acid-containing polynaphthoquinones upon the nature of Lewis acids (the perturbation of the C═O stretching frequency) (7) at 200°C: (1) the metal-free polynaphthoquinone (Q), (2) Q-$CuCl_2$, (3) Q-$ZnCl_2$, (4) Q-$FeCl_3$, (5) Q-VCl_3, (6) Q-$MoCl_5$, Lewis acid content = 7 mol%, initial pressure of ethyl alcohol = 2.0 cm Hg.

Thus the selectivity of the reaction on the polynaphthoquinone is controlled by modifying the polynaphthoquinone as well as by changing the nature of Lewis acids added to the polynaphthoquinone.

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