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Reaction Mechanism for Styrene Synthesis Over Polynaphthoquinone

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The styrene synthesis from ethylbenzene over polynaphthoquinone was investigated in the range of temperature 170–270°C. The formation of styrene on the polynaphthoquinone was observed even at 170°C. No evolution of hydrogen was found in the dehydrogenation reaction. The dehydrogenation was explained as the hydrogen transfer reaction from ethylbenzene to the quinone monomer. The catalytic activities of the modified polynaphthoquinone in styrene formation were also discussed.

The dehydrogenation of ethylbenzene to form styrene has been studied extensively over metal oxide catalysts with various additives (*1*). The dehydrogenation of ethylbenzene accompanied by the evolution of hydrogen is, in general, not appreciable below 300°C because of coming to equilibrium of the reaction. Accordingly, styrene formation from ethylbenzene over those catalysts has been studied at temperatures higher than 400°C in the presence of water or oxygen in order to overcome the restriction of the thermodynamic equilibrium.

Polynaphthoquinone, a quinone type polymer, obtained by oxidation of 1,7-naphthalenediol, has been found to function as an effective catalyst (*2*) for dehydrogenations of formic acid, alcohols, cyclohexene and ammonia, in the range of room temperature to 300°C. The organic polymers containing quinone groups which act as active sites in the dehydrogenations (*3*), are considered to have a well-defined uniform surface. It is known that the quinone compounds combine with various metal ions to form chelate complexes. The polynaphthoquinone may be regarded as the model organic polymer, the quinone compounds like coenzyme-Q, vitamin K_3, etc., playing an important role in living organisms.

Accordingly, it is of great interest to investigate the catalytic dehydrogenation of ethylbenzene over polynaphthoquinone. The present experiment indicated that the formation of styrene from ethylbenzene over the catalyst took place even below 200°C in the presence of oxygen and its selectivity was found to be almost 100%. The mechanism of the dehydrogenation was studied in comparison with metal oxide catalysts. The catalytic activities of the polynaphthoquinones containing $FeCl_3$, Pd, KOH, and Al_2O_3 were compared with that of the metal free polynaphthoquinone in the styrene formation.

EXPERIMENTAL METHODS

As was previously reported (*2*), the polynaphthoquinone (Q) is easily obtained by oxidation of 1,7-naphthalenediol with nitric acid in air, followed by treating at 350°C for 12 hr. The mixed catalysts of the polynaphthoquinone with silica (SiO_2–Q) and with alumina (Al_2O_3–Q) were prepared from known amounts of the polynaphthoquinone and a colloidal silica or an alumina-sol, respectively. The alkaline polynaphthoquinone (KOH–Q) was formed by the doping method from the polynaphthoquinone and a KOH aqueous solution. The palladium-supported polynaphthoquinone (Pd–Q) was obtained from the polynaphthoquinone and an acidic solution of $PdCl_2$ followed by removing the solvent by evaporation. The polynaphthoquinone containing $FeCl_3$ ($FeCl_3$–Q) was formed by mixing the ethyl alcohol solution of 1,7-naphthalenediol and the $FeCl_3$ aqueous solution. The $FeCl_3$ coordinates to quinone groups in the $FeCl_3$–Q catalyst (*2*). The catalysts thus obtained, Q, SiO_2–Q, Al_2O_3–Q, and KOH–Q, heated at 350°C for 1 hr in air prior to each run, while the $FeCl_3$–Q catalyst was heated at 250°C for 1 hr. The Pd–Q catalyst was reduced in hydrogen at 300°C for 7 hr.

The reactions were carried out in the range of temperature between 170 and 270°C under atmospheric pressure. The flow type apparatus was used which consisted of the glass reaction tube containing 1 g (2.5 cm^3) of the catalyst. The reactant was fed into the reactor from a microfeeder in flow of air.

The products were collected at the intervals of 20 to 30 min and analyzed by gas chromatography, using the Carbowax 1500 column for styrene, benzene and toluene. Hydrogen and carbon dioxide were analyzed, respectively, by a molecular sieve column and an active charcoal column. The Carbowax 1500 column was also used for cyclohexane, cyclohexene, cyclohexanol, and cyclohexanone.

RESULTS AND DISCUSSION

1. Various Dehydrogenation Reactions Catalyzed by the Polynaphthoquinone

As shown in Table 1, the polynaphthoquinone was found to be effective for dehydrogenation of various substrates, such as ethylbenzene, cyclohexane, cyclohexene, and cyclohexanol in the presence of oxygen. It is interesting to note that styrene was formed even at 170°C. The decomposition to form ethylene and benzene were not appreciable under the present reaction conditions and no carbon dioxide from ethylbenzene was also observed. The selectivity of the styrene formation at 200°C was almost 100%.

Cyclohexane was dehydrogenated to form benzene over the polynaphthoquinone at 300°C. Benzene was mainly produced in the dehydrogenation of cyclohexene at 200°C. The decomposition of cyclohexane and cyclohexene took place with difficulties. It is interesting to note that cyclohexene and cyclohexadiene were found in the dehydrogenation of cyclohexane and cyclohexene, respectively, because both products were regarded as intermediates in the formation of benzene from those reactants. When cyclohexanol was chosen as an example of cyclic alcohols, cyclohexanone

TABLE 1

VARIOUS DEHYDROGENATION REACTIONS CATALYZED BY THE POLYNAPHTHOQUINONE

Reactants	Temp (°C)	Space velocity (mol/g hr) ($\times 10^{-3}$)	Main products	Yields (%)	Selectivity (%)
Ethylbenzene	170	2.18	Styrene	0.9	ca. 100
	200	2.18	Styrene	2.1	ca. 100
	270	2.18	Styrene	9.1	95
Cyclohexane	300	2.5	Cyclohexene	1.8	55 } 100
			Benzene	1.5	45
Cyclohexene	200	2.5	Cyclohexadiene	0.4	16 } 100
			Benzene	2.15	84
Cyclohexanol	200	2.5	Cyclohexanone	6.3	98
			Cyclohexene	0.15	2

was predominantly formed by the dehydrogenation. A small amount of cyclohexene was also produced by the dehydration of cyclohexanol. The catalytic activity of the polynaphthoquinone remained unchanged during the reaction time studied.

No hydrogen was evolved during the reaction over the polynaphthoquinone and this is one of characteristic properties of the catalyst. Those reactions over the polynaphthoquinone were found to be completely oxidative dehydrogenations, where 2 moles of water were stoichiometrically formed from 2 moles of the substrate and 1 mole of oxygen.

2. Reaction Mechanism of Styrene Formation

The formation of styrene from ethylbenzene over the polynaphthoquinone (1 g) was studied in the range of temperature between 170 and 270°C in flow of air. The initial rates of the styrene formation obtained under the low conversions were independent of the partial pressure of ethylbenzene, as shown in Fig. 1. The adsorption amounts of ethylbenzene which were obtained by measuring pressure changes in a closed apparatus remained almost constant in the same pressure range as was used in the dehydrogenation. The initial rates of the styrene formation are also plotted against the partial pressure of oxygen in Fig. 1, from which the rates were found to be independent of the oxygen pressure in the range of 0.1 to 0.65 atm. The dehydrogenation of ethylbenzene proceeded in absence of oxygen though the formation of styrene decreased with an increase of reaction time. The initial rates of the dehydrogenation of formic acid or ethyl alcohol were much less influenced by addition of oxygen into the system (*2*). These results indicate that oxygen does not participate in the rate-determining step of the reaction. Accordingly, the rate in the initial stage of the reaction is expressed as follows: $v_0 = k(P_{eb})^0$, where v_0, k, and P_{eb} represent the rate of the styrene formation under the low conversion, the rate constant and the partial pressure of ethylbenzene, respectively. The activation energy of dehydrogenation of ethylbenzene over the catalyst was found to be 10.9 kcal/mol.

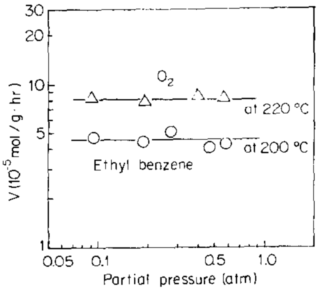


FIG. 1. The reaction rates against the partial pressures of ethylbenzene and oxygen.

When the adsorption of styrene on the polynaphthoquinone is stronger than that of ethylbenzene, the dehydrogenation of ethylbenzene would be inhibited by the styrene produced. In fact, when ethylbenzene mixed with known amounts of styrene were admitted onto the catalyst, the rate of the reaction decreased with an increase of the amounts of the added styrene.

Consequently, the rate (v) of dehydrogenation of ethylbenzene to form styrene may be expressed as follows;

$$v = k\frac{K_{eb}P_{eb}}{K_{eb}P_{eb} + K_{st}P_{st}}, \tag{1}$$

where K_{eb}, K_{st} and P_{st} are the equilibrium constant of the ethylbenzene adsorption, that of the styrene adsorption and the partial pressure of the produced styrene, respectively. The rate equation is rearranged

$$\begin{aligned}\frac{1}{v} &= \frac{1}{k} + \frac{1}{k}\frac{K_{st}}{K_{eb}}\frac{P_{st}}{P_{eb}} \\ &= \frac{1}{k} + \frac{C}{k}\frac{P_{st}}{P_{eb}},\end{aligned} \tag{2}$$

where C is equal to K_{st}/K_{eb}.The inhibiting effect of styrene on the rate of the ethylbenzene dehydrogenation was studied by adding certain amounts of styrene into the system. The reciprocal of the rates is plotted against P_{st}/P_{eb} in Fig. 2, where straight lines are found as expected in the Eq. (2).

The values of the rate constants, k, at various temperatures were obtained from the values of $1/v$ at $P_{st}/P_{eb} = 0$ in Fig. 2, the ordinates being equivalent to the reciprocal of k. The activation energy of the reaction was calculated to be 10.6 kcal/mol from Fig. 3. The value was in a good agreement with that obtained from the rates under the low conversions. The logarithms of the K_{st}/K_{eb} are also plotted against the reciprocal of temperatures in Fig. 3, where the slope of the straight line exhibits the difference between the heat of adsorption for styrene and that for ethylbenzene. The heat of adsorption for styrene on the polynaphthoquinones was found to be more than that of ethylbenzene by 9.5 kcal/mol.

The following equation is obtained by integrating the rate Eq. (1):

$$\frac{W}{F} = \frac{1}{k}\left\{(1 - C)x + C \cdot \ln\frac{1}{1 - x}\right\}, \quad (3)$$

where W/F, C, and x represent the contact time of the reaction, the ratio of K_{st} to K_{eb} and the conversion of ethylbenzene to styrene, respectively. The conversions of ethylbenzene are plotted against various contact times in Fig. 4. Since k and C are obtained at any temperature, the values of x can be calculated at any contact time under the experimental conditions. The solid lines in Fig. 4 show the calculated curves in a good agreement with the experimental values. Consequently, it was confirmed that the formation of styrene from ethylbenzene is expressed by the Eq. (1).

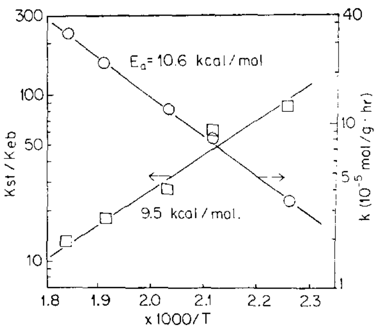


FIG. 3. The plots of the logarithms of K_{st}/K_{eb} and the rate constants (k) against $1/T$.

The rate Eq. (1) indicates that styrene is produced by the surface unimolecular reaction of the ethylbenzene adsorbed on the polynaphthoquinone.

When helium was employed as a carrier gas, the styrene formation gradually decreased with increase of reaction time and eventually the reaction ceased when the surface of the polynaphthoquinone was saturated by hydrogen from ethylbenzene.

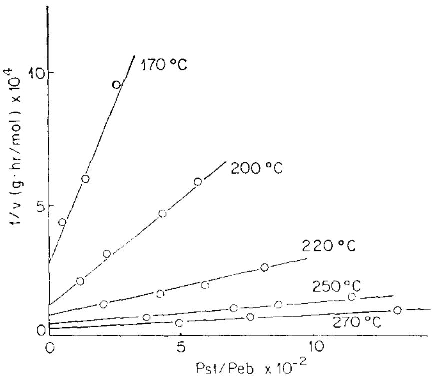


FIG. 2. The inhibiting effect of added styrene on the rate of the dehydrogenation reaction of ethylbenzene; total space velocity = 955 cm^3/g hr; (ethylbenzene + styrene) : air = 1 : 10 (molar ratio).

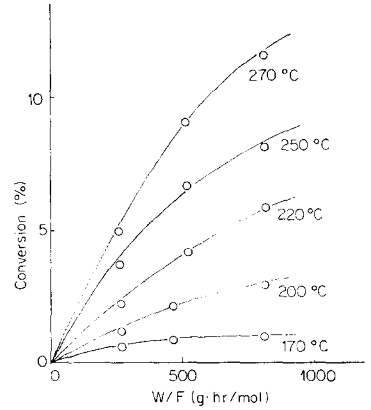
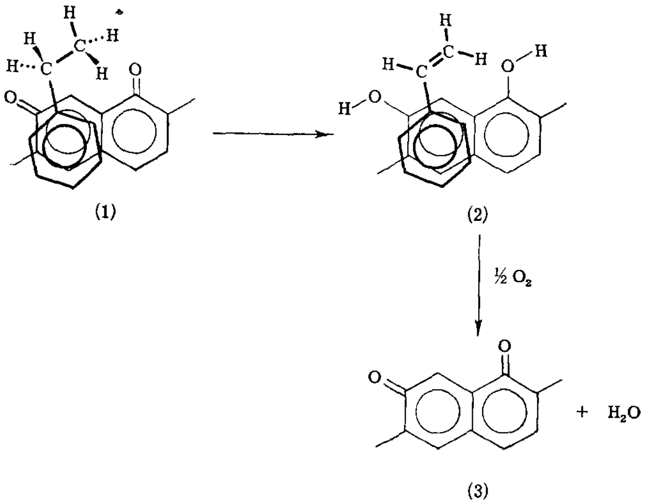


FIG. 4. The relation between the styrene formation and the contact time; calculated curves and experimental values (○).

No hydrogen was evolved during the course of the reaction. However, the catalytic activity was completely restored when oxygen is introduced to the system. This fact indicates that the catalytic dehydrogenation took place in the presence of oxygen. The typical result at 220°C is illustrated in Fig. 5. The dehydrogenation of ethylbenzene to form styrene may be explained similarly to that of ethyl alcohol; at the first step the quinone groups are reduced to form hydroquinone groups by the transfer of hydrogen from ethylbenzene and then the hydroquinone groups are rapidly oxidized to quinone groups by oxygen accompanied with the formation of water. In fact, when oxygen was introduced onto the polynaphthoquinone reduced by ethylbenzene in a closed circulating system, it rapidly reacted with the reduced catalyst to form water. Consequently, the redox reaction is repeated on the quinone groups as the active sites in the catalyst. The dehydrogenation of ethylbenzene over the polynaphthoquinone was able to be explained as the stoichiometric reaction of hydrogen transfer from ethylbenzene to the quinone monomer. This is another characteristic property of the polynaphthoquinone catalyst unlike most metal oxide catalysts.

The reaction scheme of the styrene formation from ethylbenzene may be shown as follows:



The reaction scheme of the styrene synthesis, involving a possible adsorption state of ethylbenzene on the polynaphthoquinone.

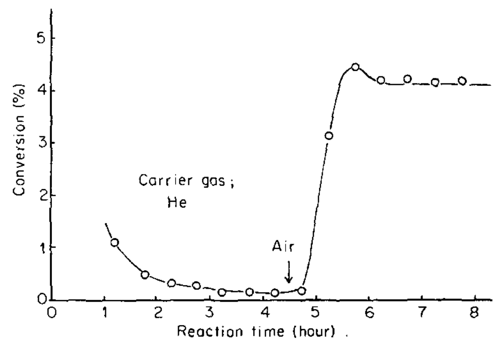


Fig. 5. The influence of oxygen on styrene formation at 220°C.

Ethylbenzene adsorbed on the catalyst may have the π–π interaction between its benzene ring and the π-conjugated system of the catalyst. It is shown in the scheme that the polynaphthoquinone acts as an effective catalyst because of its chemical and structural property.

3. Dehydrogenation of Ethylbenzene Over Various Catalysts Having Polynaphthoquinone

The catalytic activities of various catalyst (1 g) having the polynaphthoquinone in styrene formation from ethylbenzene

TABLE 2

THE CATALYTIC ACTIVITIES OF VARIOUS CATALYSTS (1 g) HAVING POLYNAPHTHOQUINONE IN THE STYRENE FORMATION FROM ETHYLBENZENE AT 200°C

Catalysts	Compositions (%)		Styrene yields[a]		Selectivity
	Additives:	Q	(Y)	Y/Q[b]	(%)
Polynaphthoquinone (Q)	0	100	2.1%	2.1	ca. 100
SiO_2-Q	97	3	0.06	2.0	ca. 100
Al_2O_3-Q	61	39	0.75	1.92	ca. 100
KOH-Q	18	82	1.64	2.0	89
Pd-Q	10	90	3.83[c]	4.26	85[c]
$FeCl_3$-Q	15	85	4.57	5.38	80

[a] W/F; 458 g hr/mol.

[b] The styrene yields per unit gram of the polynaphthoquinone.

[c] The CO_2 evolution (yield; about 7.6%) being not taken into consideration.

was studied at 200°C using a conventional flow apparatus. The results are given in Table 2. The styrene formation from ethylbenzene decreased by mixing SiO_2 and Al_2O_3 with the polynaphthoquinone, where only the effect of dilution by the additives was observed. The reactivity of the polynaphthoquinone was not influenced by treating the polynaphthoquinone with KOH. In fact, the styrene yield per gram of the polynaphthoquinone remained unchanged, independent of addition of KOH to the catalyst. However, the formation of styrene was accelerated by a factor of about 2 by adding Pd and $FeCl_3$ to the polynapthoquinone. When the Pd–Q catalyst containing 10 mol% of Pd was employed, considerable amounts of carbon dioxide were observed in the gas phase. Ethylbenzene may be oxidized to carbon dioxide on Pd metal contained in the Pd–Q catalyst (*4*). The reactivity of the quinone groups in the polynaphthoquinone was markedly affected by the addition of $FeCl_3$, where the styrene yield per unit gram of the polynaphthoquinone increased by a factor of 2.5. It should be noted that the $FeCl_3$–Q catalyst showed the high catalytic activity in the styrene synthesis from ethylbenzene.

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