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# Mechanism of the Side-Chain Alkylation of Toluene with Methanol

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The side-chain alkylation of toluene with methanol has been studied experimentally and a detailed mechanism of the reaction has been investigated by using quantum chemistry. Experimental results have shown that this reaction proceeds consecutively; styrene is primarily formed by the reaction of toluene with formaldehyde produced by the dehydrogenation of methanol, followed by the hydrogenation of styrene to form ethylbenzene. The quantum chemical calculations have shown that the presence of a basic site is indispensable to the side-chain alkylation of toluene, whereas the benzene-ring alkylation of toluene takes place on an acidic site, in accordance with experiments. Furthermore, the calculations have indicated that specific configurations of acidic and basic sites with steric restrictions are required for the side-chain alkylation of toluene. This might explain the experimental results that alkali-cation-exchanged X and Y zeolites exhibit a higher activity for this alkylation compared to the other catalysts employed.

## INTRODUCTION

Alkylation of toluene with methanol, in which toluene is selectively converted to xylenes or to a mixture of styrene and ethylbenzene, has been investigated. It is known that the benzene-ring alkylation of toluene with methanol to produce xylenes is catalyzed by solid acids, such as silica–alumina (*1*) and multivalent-cation-exchanged zeolites (*2*), while the side-chain alkylation to form a mixture of styrene and ethylbenzene occurs on catalysts with basic properties, such as alkali-cation-exchanged X and Y zeolites (*3–5*) and MgO, MgO–$TiO_2$, CaO–$TiO_2$, and $TiO_2$ (*6*). It is of great interest that the selectivity of the alkylation of toluene with methanol significantly changes with the nature of catalysts, that is, the acidic and basic properties of catalysts.

Sidorenko *et al.* (*3*) have proposed the following scheme of the side-chain alkylation of toluene with methanol:

$$CH_3OH \rightarrow HCHO + H_2 \quad (HCHO \rightarrow CO + H_2), \quad (1)$$

$$C_6H_5CH_3 + HCHO \rightarrow C_6H_5CH{=}CH_2 + H_2O, \quad (2)$$

$$C_6H_5CH{=}CH_2 + H_2 \rightarrow C_6H_5CH_2CH_3. \quad (3)$$

First, in reaction (2), styrene is formed by the reaction of toluene and formaldehyde produced by reaction (1), which is the dehydrogenation of methanol. Then, in reaction (3), styrene is hydrogenated to ethylbenzene with $H_2$ produced by reaction (1). In the reaction of hydrocarbons, such as the oxidation of propylene (*7*) and ammoxidation of toluene (*8*), however, the reactions are considered to be initiated by the dissociation of C–H bonds of methyl groups of hydrocarbons, suggesting the possibility of the following alternative mechanism of the formation of styrene in the side-chain alkylation of toluene: The dissociation of C–H bonds of the methyl



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group of toluene is followed by the reaction of methanol with the intermediate species derived from toluene. In this regard, some experiments were carried out to establish the mechanism of the side-chain alkylation of toluene with methanol.

Recently, quantum chemistry has remarkably progressed and has also been applied to the study of the heterogeneous catalyses (*9*). Concerning the heterogeneous acid–base catalyses, some studies which include the alkylation of toluene with formaldehyde on the acidic catalysts (*10*), the acidity of the halogenated silica gel (*11*), the role of the basic site for the isomerization of olefins (*12*), and the acid–base property of metal-cation-exchanged silica gel (*13*) have been reported. It is known that, in the alkylation of toluene with methanol, the alkylating reagent attacks selectively to the carbon of the benzene ring on acidic catalysts and to the side chain of toluene on basic catalysts (*1–6*). From the experimental results obtained in this study, the importance of the crystal structure of catalysts will further be suggested. Thus, the alkylation of toluene with methanol contains some new points, which can be clarified by using quantum chemistry, namely, the roles of both acidic and basic sites in the catalysis, those of the crystal structure of catalysts, and the detailed mechanism of the reaction. In other words, this reaction provides a good example where the applicability of quantum chemistry to the analysis of the mechanism of a reaction catalyzed by the solid acidic and basic sites arranged with appropriate steric configuration can be judged.

In this study, the mechanism of the side-chain alkylation of toluene with methanol has been experimentally investigated. At the same time, quantum chemical calculations have been made on the basis of the experimental results. The calculations have suggested that this kind of approach is promising for the clarification of the functions of acidic and basic sites, and of the steric factors in the catalysis.

## I. EXPERIMENTAL

### METHODS

#### *Materials and Catalysts*

Toluene and methanol, having purities of 97 and 99.5%, respectivley, were obtained from a commercial source. Potassium-cation-exchanged zeolites obtained from X, Y, A, and mordenite type zeolites were prepared by a conventional cation-exchange procedure using a 0.5–1 *N* aqueous solution of potassium chloride. KX–Pd (0.1 wt%) and KX–Cu (1 wt%) were prepared by impregnating KX with $PdCl_2$ and $CuCl_2$ solutions, respectively. Si/Al–K–Cu catalyst was prepared by impregnating silica–alumina with an aqueous solution containing KOH and $CuCl_2$. Before all the catalysts were used, they were pelleted without a binder, crushed and sized in a 28–48 mech, and then calcined at 500°C in $N_2$ stream for 3 hr.

#### *Analysis*

The reaction mixture was analyzed by gas chromatography using a 4-mm × 4-m stainless-steel column with Benton 34 (7 wt%) and DNP (5 wt%) on Celite 545 for the liquid products at 95°C and Porapak Q and molecular sieve 13X for the gaseous products at room temperature. The carrier gas for both columns was hydrogen.

#### *Apparatus and Procedure*

*1. Flow reaction technique.* Experiments were carried out with a fixed-bed reactor at atmospheric pressure. Before reaction, the catalyst was calcined at 500°C in $N_2$ stream for 3 hr and brought to the reaction temperature *in situ*. A mixture of toluene and methanol was fed by using microfeeder and carried by $N_2$ to the catalyst bed. The products were cooled and periodically collected with an ice trap, and then analyzed by gas chromatography. Residual gaseous products were collected with a syringe and were also analyzed by gas chromatography. The yields of the products and $W/F$, which is a measure of

contact time, were defined respectively as follows:

$$\text{yield (\%)} = \frac{\text{moles of products}}{\text{moles of fed methanol}} \times 100,$$

$$W/F\ (\text{g} \cdot \text{hr/mol}) = \frac{\text{catalyst weight (g)}}{\text{feed rate of reactants (toluene + methanol)(mol/hr)}}.$$

*2. Pulse reaction technique.* The 0.25-g catalyst was calcined at 500°C in He stream for 3 hr before it was used. The flow rate of carrier gas, He, was 30 ml/min.

## RESULTS

### *Activities of Various Catalysts*

Activities of various types of potassium-cation-exchanged zeolites for the side-chain alkylation of toluene with methanol are shown in Table 1. Respective yields of styrene and ethylbenzene were 7.4 and 7.1% on KX catalyst and 0.7 and 0.6% on KY catalyst. Taking into account the difference in the contact time, these results are consistent with the data reported by Yashima *et al.* (*4*). Both KA and KM zeolites gave 0.3% yield of ethylbenzene, but styrene was not produced on these catalysts. Si/Al–K–Cu catalyst showed no activity for this reaction.

### *Effect of Metals Supported on KX Zeolite*

In the case of Cu supported on KX, the yield of ethylbenzene increased slightly, while that of styrene decreased. The activity of the KX catalyst for the side-chain alkylation of toluene was markedly decreased by supporting Pd on the catalyst. Whereas, by supporting Cu or Pd on KX catalyst, the yield of CO + $CO_2$ was increased.

TABLE 1

Activities of Potassium-Cation-Exchanged Zeolites for the Alkylation of Toluene[a]

| | KX | KY | KA | KM | Si/Al–K–Cu |
|---|---|---|---|---|---|
| Yield (%) | | | | | |
| Ethylbenzene | 7.1 | 0.6 | 0.3 | 0.3 | 0.0 |
| Styrene | 7.4 | 0.7 | 0.0 | 0.0 | 0.0 |
| $SiO_2/Al_2O_3$ | 2.5 | 5.0 | 2.0 | 9–10 | 5.1 |
| Cavity diameter (Å) | 7.4 | 7.4 | 4.2 | 6.7 | — |

[a] Reaction conditions: temperature, 425°C; $W/F$, 40 g · hr/mol; $N_2/F$, 5.0 mol/mol; toluene/methanol, 6.0 mol/mol.

### *Effect of the Addition of $O_2$*

Yields of styrene and ethylbenzene decreased rapidly with increasing $O_2$ concentration up to $O_2$/methanol ratio of 1.0 and were constant above this ratio. In addition, benzene was also formed in the presence of $O_2$, and the yield of benzene increased gradually with increasing $O_2$/methanol ratio.

### *Effect of Pulse Intervals*

The effect of the intervals between methanol and toluene pulses on the yields of styrene and ethylbenzene was examined by using the pulse reaction technique (Fig. 1). The ratio of the yield of styrene to that of ethylbenzene was much larger than that with the flow technique. When pulsing methanol before the toluene pulse, ethylbenzene disappeared when the interval exceeded 5 sec. In the reverse order of the pulses, both ethylbenzene and styrene were formed up to 15 sec of the interval.

## DISCUSSION

### *Activities and Crystalline Structures of Catalysts*

It is known that alkali-cation-exchanged X-type zeolites are useful catalysts for the side-chain alkylation of toluene with methanol. The order of activities of various zeolites was KX > KY > KA, KM as shown in Table 1. On KX catalyst, yields of styrene

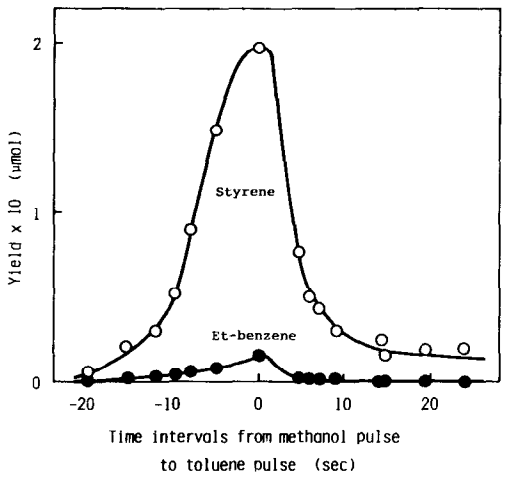


FIG. 1. Effect of pulse intervals on yields. Reaction conditions: catalyst, KX; catalyst weight, 251 mg; reaction temperature, 425°C; pulse size of methanol, 0.2 μl; pulse size of toluene, 1.0 μl.

and ethylbenzene were 7.4 and 7.1%, respectively. On both KA with a smaller cavity and KM composed of a honeycomb structure with a pore of ca. 7 Å in diameter, only ethylbenzene was produced in a yield of as low as 0.3%. Furthermore, basic catalysts without a regular crystalline structure, such as MgO, $MgO–TiO_2$, $CaO–TiO_2$, and $TiO_2$ (*6*), have been reported to show very little activities for the side-chain alkylation of toluene with methanol. From the above-mentioned data, the regular crystalline structure with a cavity such as that in KX catalyst is considered to be very important for the side-chain alkylation of toluene with methanol, although the acidic site on the catalysts also plays an important role in this reaction as will be mentioned below.

*Reaction Pathway*

In the side-chain alkylation of toluene with methanol, toluene is converted to both styrene and ethylbenzene. The formation process of these products, however, has not been clarified satisfactorily. Therefore, it was examined whether this reaction occurs consecutively or concurrently and which product is a primary one if consecutively.

One of the advantages of the pulse reaction technique is that, since components of reactants and products are inclined to be separated from one another in the pulse reactor (*14*), a primary product is more easily confirmed compared to the flow reaction technique. As shown in Fig. 1, the yield of styrene obtained by using the pulse technique was much higher than that of ethylbenzene, while, as shown in Table 1, yields of styrene and ethylbenzene obtained by using the flow technique were nearly equal to each other. The results suggest that this reaction takes place consecutively; styrene is primarily formed and then it is hydrogenated to form ethylbenzene. Sidorenko *et al.* (*3*) and Yashima *et al.* (*4*) have also suggested the same reaction scheme.

Although both methanol and formaldehyde can react with toluene to form styrene and ethylbenzene, formaldehyde has been found to be more reactive than methanol and to yield more styrene than ethylbenzene (*4*). By using infrared spectroscopy, it has also been found that formaldehyde is formed during methanol decomposition of alkali-cation-exchanged X-type zeolites (*15*). These results suggest that formaldehyde is the true alkylating reagent of toluene to form styrene, the primary product, and when methanol is used as a reactant, formaldehyde produced by the dehydrogenation of methanol acts as the alkylating reagent in the reaction.

As mentioned above, styrene is considered to be formed according to reaction (4):

$$CH_3OH \xrightarrow{-H_2} HCHO,\ HCHO + \phi CH_3 \rightarrow \phi CH{=}CH_2 + H_2O. \quad (4)$$

However, an alternative mechanism shown in reaction (5) should be ruled out in order to establish reaction (4):

$$\phi CH_3 \xrightarrow{-H_2} (\phi CH)_{ad},\ (\phi CH)_{ad} + CH_3OH \rightarrow \phi CH{=}CH_2 + H_2O, \quad (5)$$

where $(\phi CH)_{ad}$ represents an adsorbed spe-

cies of toluene. In this species, hydrogen atoms of the methyl group of toluene are abstracted. If the alkylation of toluene proceeds according to reaction (5), it would be expected that the promotion of hydrogen abstraction from the methyl group of toluene should increase the rate of this reaction. Neither addition of metals with dehydrogenation activities to KX catalyst nor that of oxygen to the reaction system promoted the alkylation of toluene. It is thus considered that the side-chain alkylation of toluene does not proceed according to reaction (5) but proceeds according to reaction (4). In order to investigate further details of the mechanism of the alkylation of toluene with formaldehyde or methanol, quantum chemical calculations were carried out as described in the next part.

## II. QUANTUM CHEMICAL CALCULATIONS

### Method of Calculations

MINDO/2 calculations (*16*) were done for the following five systems in order to study the details of the mechanism of the side-chain alkylation of toluene with formaldehyde or methanol.

(i) alkylating reagents, $CH_3OH$ and HCHO;
(ii) toluene interacting with acidic site, toluene–$H^+$ system;
(iii) toluene interacting with basic site, toluene–$OH^-$ system;
(iv) toluene interacting with both acidic and basic sites, toluene–$H^+$–$OH^-$ system;
(v) reaction between adsorbed toluene and formaldehyde.

The geometries of all five systems are illustrated in the proper figures of this part. In this calculation, acidic and basic sites were substituted by $H^+$ and $OH^-$, respectively, for simplicity of computations. This approximation has also been made in many studies [e.g., (*10, 12*)]. The reactivity of each carbon atom of toluene and formaldehyde was judged from the frontier electron density of the atom (*17*).

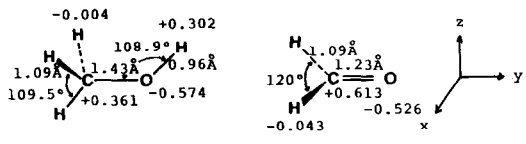


FIG. 2. Charge distributions and geometries of methanol and formaldehyde.

TABLE 2

Energy, Charge Distribution, and Frontier Electron Density (LUMO) of Formaldehyde

| | HCHO | HCHO + $H^+$ [a] | HCHO + $OH^-$ [b] |
|---|---|---|---|
| Energy of formaldehyde (eV): | −471.4 | −477.9 | −469.9 |
| Charge distribution | | | |
| $H_F$ | −0.043 | +0.098 | −0.193 |
| $C_F$ | +0.613 | +0.730 | +0.853 |
| $O_F$ | −0.526 | −0.284 | −1.000 |
| $F_r^{(n)}$ of $C_F$ | | | |
| $P_x$ | 0.000 | 0.000 | 0.000 |
| $P_y$ | 0.000 | 0.001 | 0.104 |
| $P_z$ | 1.346 | 1.664 | 0.000 |

[a] $H^+$ interacts with the oxygen atom of HCHO and the $H^+$–O distance is 0.96 Å.
[b] $OH^-$ interacts with the carbon atom of HCHO and the $OH^-$–C distance is 1.43 Å.

### Results and Discussion

#### *Reactivity of Formaldehyde Adsorbed on Acidic or Basic Site*

Formaldehyde is considered to act as the true alkylating reagent in the alkylation with methanol as shown in Part I. In accordance with the mechanism, the MINDO/2 calculations indicated that formaldehyde is more reactive than methanol, because the carbon atom of formaldehyde is more positive than that of methanol (Fig. 2).

The reactivity of formaldehyde is changed by the interaction with the acidic or basic site on the catalyst. Table 2 shows the energy of formaldehyde, the charge distribution in formaldehyde interacting with the acidic or basic site, and electron densities of the lowest unoccupied molecular orbital (LUMO), that is, frontier electron densities of formaldehyde for the nucleophilic reaction [$F_r^{(n)}$]. The charge on the carbon atom of formaldehyde interacting

with $H^+$ or $OH^-$ is more positive than that of free formaldehyde. This result suggests a higher nucleophilic reactivity of formaldehyde when interacting with the acidic or basic site. Furthermore, adsorption of formaldehyde on the acidic site of the catalyst results in the larger $F_r^{(n)}$ value of the carbon atom and the lower energy of formaldehyde, whereas that on the basic site results in the lower $F_r^{(n)}$ value and the higher energy. In other words, the nucleophilic reactivity of formaldehyde is enhanced by interacting with the acidic site of the catalyst and it can be stably adsorbed on the acidic site.

*Interaction of Toluene with the Acidic Site ($H^+$)*

The configuration of toluene interacting with the acidic site under the center of the benzene ring was considered as shown in Fig. 3. By using the extended Hückel method, Ohkubo *et al.* (*10*) have reported that the toluene–$H^+$ system with $H^+$ situated at the (a) position in Fig. 3 was the most stable. However, in the present study using the MINDO/2 method, the toluene–$H^+$ system was calculated to be most stable when $H^+$ interacts with toluene at the (b) position, that is, with the benzene ring of toluene. Therefore, further calculations were done for this configuration of the toluene–$H^+$ system. Figure 4 shows the change in the energy of toluene in this system against $r_{H+}$ and the lowest energy of toluene which can be found at $r_{H+}$ of 0.95 Å. This indicates that toluene chemisorbs most stably on the acidic site at this distance. Electron densities of the highest

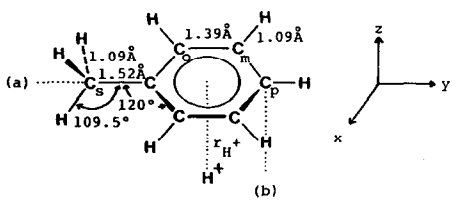


FIG. 3. Geometry of toluene–$H^+$ system. $r_{H+}$ is the distance from the center of the benzene ring to the acidic site, $H^+$.

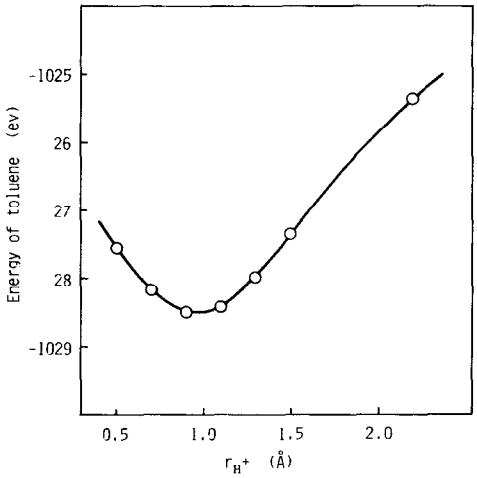


FIG. 4 Change in the energy of toluene in toluene–$H^+$ system with $r_{H+}$. Toluene interacts with $H^+$ under the center of the benzene ring shown in Fig. 3.

occupied molecular orbital (HOMO), that is, frontier electron densities for the electrophilic reaction [$F_r^{(e)}$], were calculated and are shown in Table 3 in order to determine the most active position in toluene for the electrophilic reaction. As shown in Table 3, the $F_r^{(e)}$ of the carbon atoms of the benzene ring of toluene are larger than that of the side chain. Among carbon atoms of the benzene ring, carbons of *para* and *ortho* positions show larger values of $F_r^{(e)}$ than *meta* carbons. From the results of the $F_r^{(e)}$ of the carbon atoms and the above-mentioned stability of the toluene–$H^+$ system, it is considered that, on the acidic site, carbon atoms of the benzene ring of toluene are likely to be attacked by an electrophilic reagent. This explains well the experimental result that, on the solid acid catalysts, the alkylation of toluene with methanol (*1, 2*) or formaldehyde (*18*) takes place on the benzene ring of toluene.

*Interaction of Toluene with the Basic Site ($OH^-$)*

Calculations were done for four different configurations of the toluene–$OH^-$ system shown in Fig. 5. When toluene interacts with $OH^-$ at the (a) position, the system was calculated to be most stable. There-

TABLE 3

Energy and Frontier Electron Density (HOMO) of Toluene

| | Toluene | Toluene + $H^+$ | Toluene + $OH^-$ | Toluene + $H^+$ + $OH^-$ |
|---|---|---|---|---|
| $r_{H^+}$ (Å): | — | 0.90 | — | 0.95 |
| $r_{OH^-}$ (Å): | — | — | 1.35 | 1.35 |
| Energy of toluene (eV): | −1022.5 | −1028.5 | −1023.0 | −1033.5 |
| | | Frontier electron density (HOMO) $F_r^{(e)}$ | | |
| $C_o$ $P_x$ | 0.000 | 0.000 | 0.002 | 0.002 |
| $P_y$ | 0.000 | 0.000 | 0.003 | 0.001 |
| $P_z$ | 0.205 | 0.199 | 0.121 | 0.095 |
| $C_m$ $P_x$ | 0.000 | 0.000 | 0.000 | 0.000 |
| $P_y$ | 0.000 | 0.000 | 0.003 | 0.002 |
| $P_z$ | 0.124 | 0.122 | 0.001 | 0.001 |
| $C_p$ $P_x$ | 0.000 | 0.000 | 0.000 | 0.000 |
| $P_y$ | 0.000 | 0.001 | 0.000 | 0.001 |
| $P_z$ | 0.602 | 0.611 | 0.125 | 0.152 |
| $C_s$ $P_x$ | 0.000 | 0.000 | 0.000 | 0.000 |
| $P_y$ | 0.000 | 0.000 | 0.099 | 0.077 |
| $P_z$ | 0.057 | 0.106 | 0.740 | 0.721 |

fore, detailed calculations were carried out for this position. Figure 6 shows the change in the energy of toluene in this system against $r_{OH^-}$. The energy of toluene is lowest at the $r_{OH^-}$ of 1.50 Å, but the difference in the energy of toluene between the toluene–$OH^-$ system and free toluene is not large, showing that toluene is not stabilized enough by the interaction with the $OH^-$ site. Calculated $F_r^{(e)}$ values of the carbon atoms of toluene in this system are shown in Table 3. Contrary to the case of the toluene–$H^+$ system, $F_r^{(e)}$ of the side-chain carbon atom of toluene is larger than that of any other carbon atoms in the benzene ring of toluene, suggesting that the basic site is necessary for the side-chain alkylation of toluene. This is in accordance with experimental results, since the activities of catalysts for the side-chain alkylation of toluene with methanol or formaldehyde are correlated to the basicities of the catalysts (*4, 6*). It seems difficult, however, to consider that the side-chain alkylation of toluene is catalyzed by the basic site alone. This is because, as mentioned above, toluene cannot be adsorbed enough on the basic site.

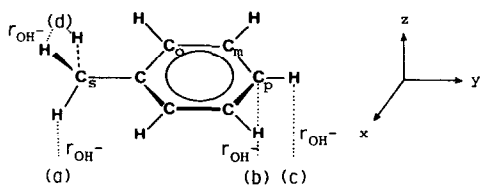


FIG. 5. Position of $OH^-$ in toluene–$OH^-$ system. $r_{OH^-}$ is the distance from H atoms to the basic site, $OH^-$. (a), (b), (c), and (d) indicate $OH^-$ positions.

### *Interaction of Toluene with Both Acidic and Basic Sites*

In the above-mentioned calculations, it has been shown that the benzene-ring alkylation is catalyzed by the acidic site alone, but that the side-chain alkylation is not promoted by the basic site alone, although the presence of the basic site is indispensable to the side-chain alkylation of toluene. Alkali-cation-exchanged zeolites have been reported to exhibit acidic property for the decomposition of 2-propanol (*19*), although these zeolites have been shown to have no acidic site by using the infrared study of the adsorption of pyridine (*20*). Therefore, cal-

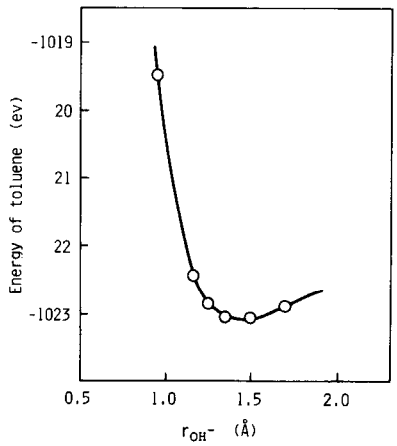


FIG. 6. Change in the energy of toluene in toluene–$OH^-$ system with $r_{OH^-}$. Toluene interacts with $OH^-$ at the (a) position shown in Fig. 5.

culations were carried out for toluene interacting with both acidic and basic sites as shown in Fig. 7 where $r_{H^+}$ and $r_{OH^-}$ are respectively 0.95 and 1.35 Å. At this configuration, the system was calculated to be most stable. As shown in Table 3, $F_r^{(e)}$ values of the various carbon atoms of toluene interacting with both $H^+$ and $OH^-$ change similarly to those of toluene interacting with $OH^-$ alone, indicating that the side-chain carbon atom has higher reactivity than the benzene-ring carbon atoms in both systems. It should be noted in Table 3 that the energy of toluene in the system of toluene, $H^+$, and $OH^-$(−1033.5 eV) is significantly lower than that composed of toluene and $OH^-$(−1023.0 eV), which means that the acidic site stabilizes the system by interacting with the benzene ring of toluene. Consequently, in the side-chain alkylation of toluene, a cooperative action of acidic and basic sites is considered to be of great importance. Noting the $F_r^{(e)}$ values of the $p_x$, $p_y$, and $p_z$ orbitals of the side-chain carbon atom, it is suggested that the alkylating reagent attacks the methyl group of toluene from the direction of $z$ axis, that is, perpendicularly to the adsorption plane of toluene, since the $F_r^{(e)}$ value of the $p_z$ orbital is much larger than those of the $p_x$ and $p_y$ orbitals as shown in Table 3.

*Roles of Acidic and Basic Sites in the Alkylation of Toluene with Formaldehyde*

As mentioned above, the cooperative action of acidic and basic sites is important in the side-chain alkylation of toluene. Here, individual roles of the acidic and basic sites are discussed. In toluene alone, as shown in Table 3, $F_r^{(e)}$ values of the carbon atoms in the benzene ring of toluene are larger than that of the carbon atom of the methyl group, thus showing that the benzene ring of toluene is more reactive in the reaction. In toluene interacting with $H^+$, individual $F_r^{(e)}$ values are similar to those of toluene alone, while the energy of toluene in the toluene–$H^+$ system is lower than that of toluene alone, indicating the smooth adsorption of toluene on the acidic site. Interaction of toluene with $OH^-$ makes the carbon atom of the side chain of toluene more reactive than those of the benzene ring, although toluene is not fully stabilized by the interaction. When the toluene–$OH^-$ system further interacts with $H^+$, that is, in the toluene–$H^+$–$OH^-$ system, the energy of toluene is significantly lowered, while individual $F_r^{(e)}$ values of the carbon atoms are almost the same as those of the toluene–$OH^-$ system but different from those of the toluene–$H^+$ system. Consequently, the roles of acidic and basic sites in the side-chain alkylation of toluene with formaldehyde can be summarized as follows: The basic site determines the selectivity of the side-chain alkylation of toluene by interacting with the methyl group of toluene, whereas the acidic site adsorbs and stabilizes toluene by interacting with the benzene ring of toluene.

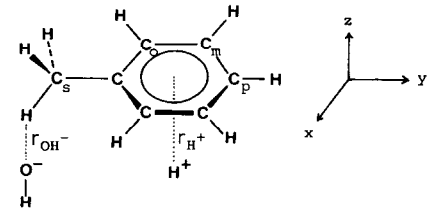


FIG. 7. Geometry of toluene–$H^+$–$OH^-$ system. $r_{H^+}$, 0.95 Å; $r_{OH^-}$, 1.35 Å.

*Reaction of Formaldehyde and Toluene Adsorbed on Both Acidic and Basic Sites*

In order to investigate the details of the reaction of adsorbed toluene and formaldehyde, calculations were made for the eight states during the course of the reaction shown in Fig. 8. In the initial state (state 1), the distance between adsorbed toluene and formaldehyde is infinite. In the final state (state 8), reaction products, styrene and $H_2O$, are desorbed from the surface. Table 4 shows the total energy of each state and bond energies ($E_{AB}$) of individual bonds in these states. Bond energies ($E_{AB}$) referred to in this paper are diatomic contributions of the total energy defined by Pople and Beveridge (*21*). A negative value of $E_{AB}$ refers to the bonding interaction, while a positive one refers to the antibonding interaction. As formaldehyde approaches the methyl group of toluene (states 2–4), new bonds are formed between $C_F$ and $C_s$ atoms and between $O_F$ and $H_s$ atoms, while $C_F$–$O_F$

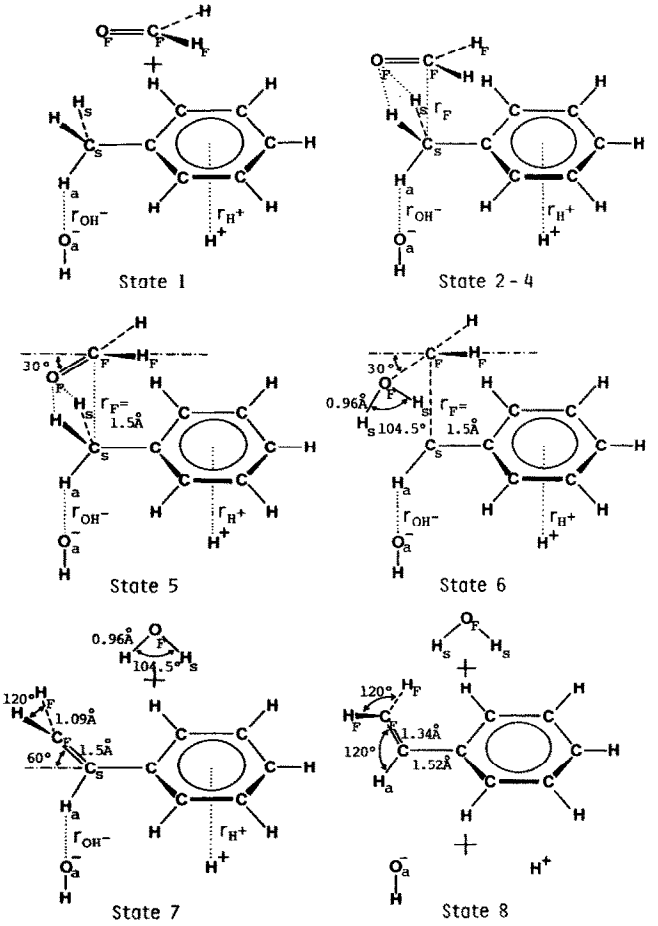


FIG. 8. States during the course of the reaction of toluene and formaldehyde. In states 1–7, $r_{H^+}$ and $r_{OH^-}$ are 0.95 and 1.35 Å, respectively. State 1 is composed of free formaldehyde and toluene interacting with both $H^+$ and $OH^-$. In states 2, 3, and 4, formaldehyde approaches the methyl group of toluene, retaining its plane parallel to the catalyst surface, at $r_F$ values of 2.00, 1.75, and 1.50 Å, respectively. In state 5, formaldehyde is rotated at 30° as shown in this figure. In state 6, two $H_s$ atoms are transferred and $H_s$–$O_F$–$H_s$ forms the configuration of water. State 7 is composed of free water and styrene interacting with both $H^+$ and $OH^-$. State 8 is composed of free water, styrene desorbed from the surface, $H^+$, and $OH^-$.

TABLE 4

Total Energy and Bond Energies ($E_{AB}$) for States in Fig. 8[a]

| State: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Total energy (eV): | −1831.7 | −1827.3 | −1825.0 | −1821.3 | −1816.6 | −1811.8 | −1828.3 | −1819.8 |
| | | | | | $E_{AB}$ (eV) | | | |
| $C_F$–$C_s$ | — | −2.523 | −5.470 | −10.079 | −9.283 | −10.001 | −17.694 | (−23.329) |
| $O_F$–$H_s$ | — | −0.106 | −1.100 | −3.013 | −7.084 | −9.402 | (−16.632) | (−16.632) |
| $C_F$–$O_F$ | (−29.750) | −28.756 | −26.899 | −23.487 | −15.663 | −13.585 | — | — |
| $C_s$–$H_s$ | −12.337 | −12.169 | −11.557 | −9.942 | −6.647 | −4.322 | — | — |
| $C_F$–$H_F$ | (−13.358) | −13.082 | −12.749 | −11.893 | −12.538 | −12.831 | −12.952 | (−13.012) |
| $C_s$–$H_a$ | −6.976 | −6.586 | −6.391 | −6.463 | −6.805 | −7.742 | −6.443 | (−12.889) |
| $H_a$–$O_a$ | −10.425 | −10.912 | −11.196 | −11.381 | −11.429 | −11.273 | −10.530 | — |

[a] The $E_{AB}$ values in parentheses indicate the energies of the corresponding bonds in free molecules, that is, formaldehyde, water, and styrene.

and $C_s$–$H_s$ bonds become weaker. Further increases in the energies of $C_F$–$C_s$ and $O_F$–$H_s$ bonds and further decreases in the energies of $C_F$–$O_F$ and $C_s$–$H_s$ bonds take place in turn in states 5–8. This shows the smooth progress of the reaction from the initial state to the final state. Noting the change in the total energy, it increases from state 1 to state 6 and decreases again at state 7. This indicates that the reaction of adsorbed toluene and formaldehyde is an activated process with a positive value of the activation energy. As shown above, the adsorption of toluene on a catalyst with both acidic and basic sites does not require the activation energy. Furthermore, the desorption energy of styrene was calculated to be smaller than the activation energy in the reaction of adsorbed toluene and formaldehyde as can be seen from Table 4. Therefore, the surface reaction of adsorbed toluene and formaldehyde may limit the rate of the side-chain alkylation of toluene with formaldehyde.

According to the present calculations in the side-chain alkylation, formaldehyde attacks the methyl group of toluene adsorbed on acidic and basic sites perpendicularly to the catalyst surface. Taking into account the enhanced nucleophilic reactivity of formaldehyde adsorbed on the acidic site (Table 2), this suggests a reaction model illustrated in Fig. 9. In this model, acidic and basic sites are located below toluene, while formaldehyde with an acidic site lies above toluene. Since the determination of the detailed position of the acidic site interacting with formaldehyde is not very easy, the effects of the acidic site interacting with formaldehyde are neglected in the states shown in Fig. 8. However, a calculation was done for a state with the acidic site located at a distance of 1.5 Å above the oxygen atom of formaldehyde (this is one of the states represented by the model shown in Fig. 9 and hereinafter called state A); the geometry of toluene, acidic and basic sites interacting with toluene, and formaldehyde is the same as that of state 2 in Fig. 8. The comparison of the calculated results for state A with those for state 2 (Table 4) showed that total energy of the system

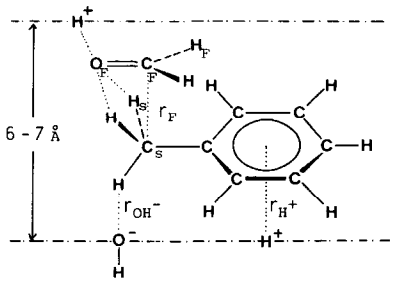


FIG. 9. Configuration of acidic and basic sites on the catalyst in the reaction of toluene and formaldehyde.

becomes lower and the $C_F$–$C_s$ bond becomes stronger by the presence of the acidic site interacting with formaldehyde. These results suggest the promotive effect of the acidic site interacting with formaldehyde on the side-chain alkylation of toluene, thus supporting the validity of the model shown in Fig. 9.

## CONCLUSIONS

The calculations have indicated that the presence of a basic site is indispensable to the side-chain alkylation of toluene but that the benzene-ring alkylation of toluene takes place on an acidic site. This is in accordance with the experiments described above. In other words, the significant change in selectivity of the alkylation of toluene due to the acidic and basic properties of the catalysts has successfully been explained by using quantum chemistry.

The present calculations also suggest the reaction model shown in Fig. 9 for the side-chain alkylation of toluene with methanol. In other words, this reaction needs specific configurations of acidic and basic sites with steric restrictions. Among the catalysts employed for the side-chain alkylation of toluene, alkali-cation-exchanged zeolites with appropriate pore structures would satisfy the steric condition. This may explain the experimental results that alkali-cation-exchanged X and Y zeolites are significantly more active than the other catalysts. Thus, the importance of the steric factor of the catalysts in the side-chain alkylation of toluene has satisfactorily been understood by using quantum chemistry.

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