Mechanisms for the Reaction of Phenol with Methanol over the $ZnO-Fe_2O_3$ Catalyst

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It was confirmed from the infrared spectra of phenol chemisorbed on $ZnO-Fe_2O_3$ that the surface species were characterized by a loss of O–H stretching (3250 cm^{-1}) and by in-plane bending vibration (1370 cm^{-1}) as well as by a phenol ring vibration (1472 cm^{-1}) and a shift of the C–O stretching mode from 1230 cm^{-1} to 1248 cm^{-1}. From these data, phenoxide surface species were proposed. Furthermore, the dissociative adsorption of phenol was discussed by taking account of the acidity and basicity of the catalyst. That is, in the case of the adsorption, phenol was thought to sit on the acid and the base site. Based on the above discussion, a mechanism for the selective methylation at the *ortho* position of phenol was proposed. On the other hand, it was found from the infrared spectrum that a surface species similar to zinc formate appears on the chemisorption of methanol. Therefore, it may be possible to consider that methanol adsorbed on the base site decomposes *via* formate-like surface species to form carbon dioxide, carbon monoxide, and hydrogen.

Phenol reacts with alcohol over solid acidic catalysts such as alumina by means of vapor phase reaction to yield ring-alkylated products.[1] However, because of its low selectivity for a desired alkylphenol, the application of the reaction has not attracted special attention in industry. Since selective alkylation is of special interest[2] (mainly *ortho*-methylation), various catalysts have been reported.[3] These catalysts consist mainly of a solid basic component, such as magnesium oxide or zinc oxide. The products by the alkylation over solid acidic catalysts and solid basic catalysts differ significantly. This interest led to an attempt to study the mechanism of the alkylation of phenol. The mechanism of alkylation was studied by Cullinane and Chard.[4] As the intermediate of alkylation, Klemm and Taylor reported on cyclohexadienone[5] and Nishizaki *et al.* reported on alcoxybenzene.[6] Recently, Nishizaki and Tanabe studied the mechanism of the methylation of phenol over alumina, silica–alumina,[7] and $MgO-Al_2O_3$.[8] Taylor and Ludlum studied the structure of phenols chemisorbed on alumina by infrared techniques.[9]

Previously, the present author found that the $ZnO-Fe_2O_3$ catalyst promoted the selective methylation at the *ortho* position of phenol with methanol and also the simultaneous decomposition of methanol.[10] It is the purpose of this paper to report the mechanisms of the *ortho*-methylation of phenol and the decomposition of methanol over the $ZnO-Fe_2O_3$ catalyst.

Experimental

Materials. Phenol and benzene of an analytical reagent grade were distilled once. Because of the high solidifying point of phenol, an equimolar solution of phenol with benzene was used for measuring the basicity. Pyridine of an analytical reagent grade was dehydrated in potassium hydroxide, distilled, and used for measuring the acidity.

Equipment. The equipment employed for measuring the basicity and the acidity of the present catalyst was a conventional gas chromatograph constructed in our laboratories (Column; Silicone Oil DC 550, 2 m, 150 °C, 7 ml/min, TCD: 80 mA). The only modification was the incorporation of a special furnace designed to hold a 40 cm U-tube, made of 3mm-i.d. stainless steel pipe. Electric heating was supplied by means of a nickelchrome wire wound on the ceramic tube; the temperature of U-tube had a deviation range of 0.2 °C. The weight of the catalyst in the bed was about 500 mg (approximately 5 cm). Before adsorption, catalyst was heated in a stream of helium gas at 400 °C for 3 hr. Then, the catalyst bed was controlled at the prescribed temperature of 200 °C and 375 °C. The chromatogram was counted by using a digital integrator of the Takeda Riken Co., Ltd.

Measurement of the Basicity and the Acidity. As the present catalyst was colored, the acidity and the basicity could not be measured by the Benesi method (indicator method). Therefore, the basicity was measured by means of the adsorption of phenol vapor,[11] while the acidity was measured by means of the adsorption of pyridine vapor.[12]

A given phenol-benzene solution was injected into the catalyst bed in the U-tube by means of a microliter injector of the Hamilton type. The peak of phenol in the chromatogram is not observed upon the initial injection, but the peak is gradually observed on successive injections and finally reaches a constant height. Thus, the irreversible adsorption of phenol, *i. e.*, the basicity, can be evaluated. Similarly, the irreversible adsorption of pyridine, *i. e.*, the acidity, can also be evaluated.

Catalysts. The catalysts ($ZnO-ZnFe_2O_4$) used for the reaction of phenol with methanol were prepared by the procedures described in a previous report.[13] The methods of preparation and the properties of the catalysts are briefly summarized in Table 1. Zinc oxide and zinc ferrite were used for observations of the adsorption of phenol and methanol. The zinc oxide (4 m^2/g) was of an analytical reagent grade, and the zinc ferrite (24.2 m^2/g) was coprecipitated by adding

TABLE 1. PREPARATIONS AND PROPERTIES OF $ZnO-Fe_2O_3$ CATALYSTS

Starting materials Zn-Fe	Calcination temperature (°C)	Surface area (m^2/g)
O-O	600	7.5
CO_3-O	600	18.8
O-OH	600	14.5
	700	8.2
CO_3-OH	500	21.2
	600	19.6
	700	5.3
OH-OH	500	36.6
	600	12.6
	700	3.3

a 14% aqueous ammonium solution to a solution containing one mole of zinc nitrate and two moles of ferric nitrate.[10]

Infrared Spectrometry of Catalysts. A double-beam infrared spectrometer (Model 402G; Japan Spectroscopic Co., Ltd.) was used for measuring the spectra in the wave-number region between 4000 cm^{-1} and 430 cm^{-1}. The *in situ* cell used for the measurement of the adsorption spectra of phenol and methanol was the same as that described previously.[16] The cell was made from quartz, and its heating was electrically supplied by means of a nickelchrome wire wound outside the quartz tube. The catalyst disk placed in the cell was heated under a vacuum (10^{-4} Torr) up to 400 °C. The disk was made in the following manner: the catalyst was ground to a fine powder (325 mesh, 44 μ), and then about 150 mg of the catalyst powder was pressed into a disk. The adsorption spectra on the catalyst disk were measured under a vacuum at room temperature.

Results

Phenol Chemisorption. Before measuring the adsorption spectra of phenol, the background spectra were measured. The zinc ferrite and the zinc oxide were heated for 3 hr under a vacuum (10^{-4} Torr) at 200 °C and then cooled to room temperature. The zinc ferrite showed a broad band at about 3100 cm^{-1}, this band may be attributed to the surface O–H stretching frequencies. However, the zinc oxide did not show the background spectrum in the wave-number region 1150 and 4000 cm^{-1}. Then, after the exposure of the disk of zinc ferrite in the cell to phenol vapor for 30 minutes at room temperature, evacuation was carried out for 3 hr at room temperature and at 100, 350, and 400 °C. Similarly, after the exposure of the disk of zinc oxide in the cell to phenol vapor for 30 minutes at room temperature, evacuation was carried out for 3 hr at 200 °C. The infrared spectra are shown in Figs. 1 and 2. A comparison of the spectra in Fig. 1 with the spectrum of phenol in KBr indicates that the phenol O–H stretching vibration (3250 cm^{-1}) and the in-plane bending vibration (1370 cm^{-1}) as well as the phenol ring vibration (1472 cm^{-1}) disappeared upon chemisorption. Furthermore, the phenol C–O stretching vibration (1230 cm^{-1}) shifts at 1248 cm^{-1}. These results are quite similar to the results of the chemisorption of phenol on alumina reported by Taylor and Ludlum.[9] Variations in the chemisorption spectra with a rise in the evacuation temperature are observed in Fig. 2. The phenol O–H stretching vibration gradually shifts from 3400 to 3150 cm^{-1} and disappears at the same time when the phenol O–H in-plane bending vibration (1390 cm^{-1}) disappears. The chemisorption spectra of phenol on zinc ferrite at 350 and 400 °C are similar to the spectrum on zinc oxide in Fig. 1. It is clear from these observations and the results of Taylor and Ludlum that the phenol molecule loses a proton on the surface and that the phenoxide anion is chemisorbed on the metal ion.

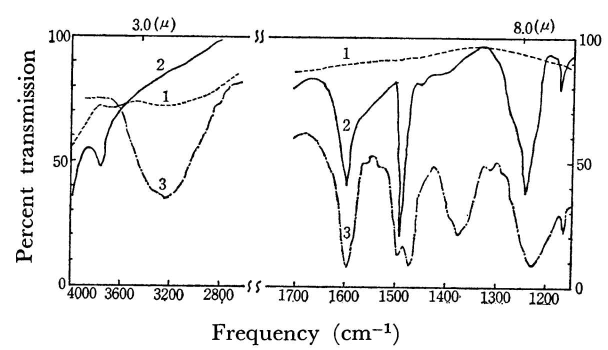

Fig. 1. Infrared spectra of phenol chemisorbed on ZnO.
(1) background, (2) phenol chemisorbed on ZnO, (3) phenol in KBr.

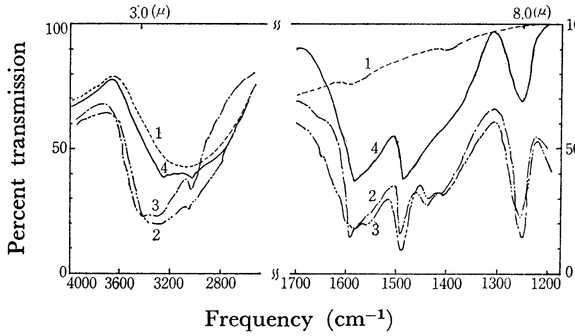

Fig. 2. Infrared spectra of phenol chemisorbed on $ZnFe_2O_4$.
(1) background, (2) phenol evacuated at 100 °C, (3) phenol evacuated at 350 °C, (4) phenol evacuated at 400 °C.

Methanol Chemisorption. Before measuring the adsorption spectrum of methanol, the background spectra were measured. The zinc ferrite and the zinc oxide were heated for 3 hr under a vacuum (10^{-4} Torr) at 200 °C and then cooled to room temperature. The background spectra of the zinc ferrite and zinc oxide were not observed in the wave-number region between 1300 and 1800 cm^{-1}. Then, the disk of zinc oxide in the cell was exposed to 30 Torr of methanol vapor for 5 minutes at 150 °C and then evacuated for 1 hr at 165, 200, and 315 °C. Similarly, the disk of zinc ferrite was also exposed to 30 Torr of methanol vapor for 5 minutes at 150 °C and then evacuated for 1 hr at 200 °C. The spectra are compared

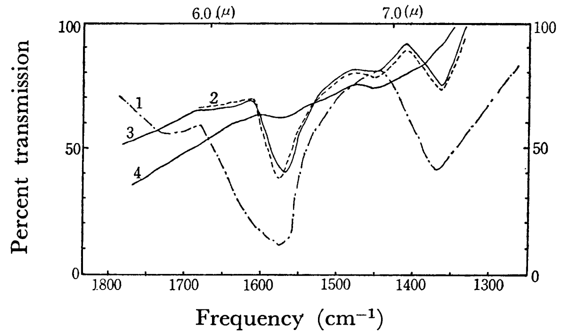

Fig. 3. Infrared spectra of methanol chemisorbed on ZnO and $ZnFe_2O_4$.
(1) zinc formate, (2) methanol evacuated at 200 °C on $ZnFe_2O_4$ (3) methanol evacuated at 165 and 200 °C on ZnO, (4) methanol evacuated at 315 °C on ZnO
* Background spectra of ZnO and $ZnFe_2O_4$ are shown in Figs. 1 and 2.

with the spectrum of zinc formate in Fig. 3. All of the spectra in Fig. 3 are quite similar to the spectrum of zinc formate. Tamaru *et al.* have reported that the methanol adsorbed on zinc oxide decomposes *via* the formate intermediate to form carbon monoxide, carbon dioxide, and hydrogen.[14] It can, therefore, be expected that the observed spectra (Fig. 3) are attributable to the intermediate of the decomposition of methanol over the present catalyst. However, no information about methylation was obtained from the present infrared spectra of methanol.

Acidic and Basic Properties. A typical relation between the acidic and basic properties of the catalyst is shown in Fig. 4. In obtaining the results in Fig. 4, we measured: (1) the saturated adsorption of pyridine on the fresh catalyst without the pre-adsorption of phenol (the acidity was 24.5 μmol/g-cat.); (2) the saturated adsorption of phenol on the fresh catalyst (the basicity was 98.5 μmol/g-cat.), and the adsorption of pyridine after the saturated adsorption of phenol (9.2 μmol/g-cat.); and (3) the adsorption of pyridine after the pre-adsorption of phenol. In those procedures, the amount of the adsorption of pyridine gradually decreased from 24.5 μmol/g-cat. to 9.2 μmol/g-cat. It is clear from these results that phenol is adsorbed on both the acid site and the base site of the catalyst.

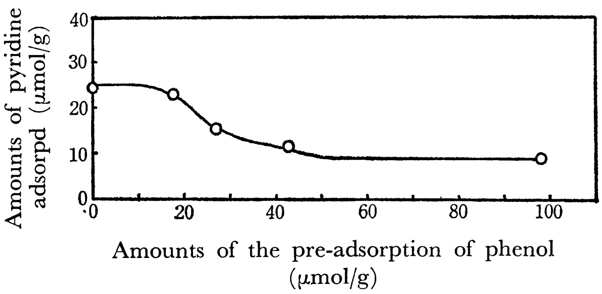

Fig. 4. Acidic and basic properties of $ZnCO_3$–$Fe(OH)_3$ calcined at 600 °C.

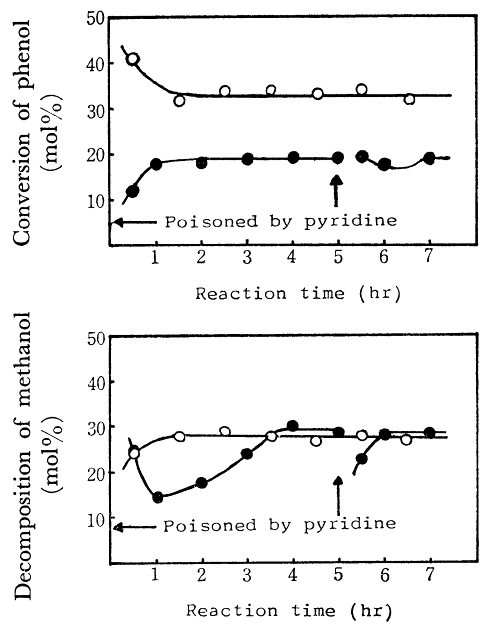

Fig. 5. Effects of poisoning by pyridine.
Reaction conditions;
W/F; 24 g-cat·hr/mol.
Reaction temp.; 375 °C
Reactants; methanol(5 mol)/phenol(1 mol)
Catalyst; From $ZnCO_3$-$Fe(OH)_3$ calcined at 500 °C
(○) Results of the reaction without poisoning by pyridine
(●) Results of the reaction after poisoning by pyridine

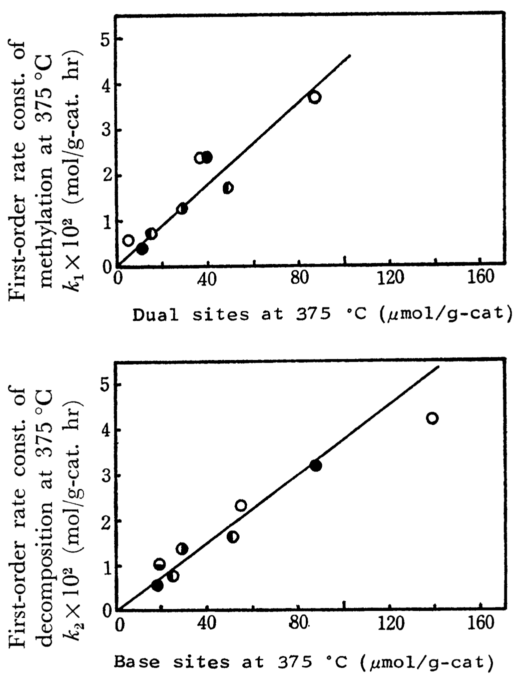

Fig. 6. Relations between rate constants and active sites of ZnO-Fe_2O_3 catalyst in several preparations. (-○-) prepared from $Zn(OH)_2$-$Fe(OH)_3$, (-●-) from $ZnCO_3$-$Fe(OH)_3$, (-◑-) from $ZnCO_3$-Fe_2O_3, (-◐-) from ZnO-$Fe(OH)_3$, (-◒-) from ZnO-Fe_2O_3.

In order to confirm the above results, the poisoning effects by pyridine were examined; the results are given in Fig. 5. The fresh catalyst was first placed in contact with small amounts of pyridine under the present reaction conditions. Then, the reaction of phenol with methanol was carried out under the same conditions. According to the experimental results, the methylation was considerably hindered by the first poisoning operation, but no further decrease in the activity occurred upon the second poisoning operation. Further, the experimental results show that the active site for the methylation is permanently poisoned by the first addition of pyridine. On the other hand, the decomposition of methanol was found to be temporarily poisoned by each operation and the activity was easily recovered. The relations between the number of active sites for the individual reaction and the first-order rate constant are given in Fig. 6. These facts seem to suggest that the methylation occurs on a dual site composed of an acid site and a base site, while the decomposition of methanol occurs only on a base site.

Discussion

With respect to the identification of the active sites for the methylation of phenol and the decomposition of methanol, the above experimental results give obvious evidence. Now, let us discuss the mechanism for the selective methylation at the *ortho* position of phenol and the decomposition of methanol. It has been reported that the methylation of phenol over alumina proceeds *via* anisole as a key intermediate.⁶⁾ However, no reaction was found to take place when only anisole vapor or a mixed vapor of anisole and methanol was placed in contact with the present catalyst. Therefore, the methylation of phenol over the present catalyst cannot be considered to proceed *via* anisole.

The selective methylation of phenol at the *ortho* position may proceed by means of the following mechanism: phenol may dissociate into the phenoxide anion and proton on the catalyst surface, and methanol may be adsorbed onto the proton to form the methyl cation.¹⁵⁾ As the distance between the phenoxide species and the proton is inevitably governed by the O–H bond length of phenol, the methyl cation may be located at a site neighboring the *ortho* position of the phenoxide species. On the other hand, Fig. 3 strongly supports the idea that the decomposition of methanol proceeds *via* formate on both zinc oxide and zinc ferrite.¹⁴⁾ Therefore, the proposed mechanism is applicable to the reactions which occur on both zinc oxide and zinc ferrite.

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