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The Alkylation of Phenol over the ZnO–Fe_2O_3 Catalyst

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Synopsis. The highly selective alkylation at the *ortho* position of phenol was caused by the dissociative adsorption of phenol; it was discussed by taking account of the acidic and the basic properties of the ZnO–Fe_2O_3 catalyst.

The catalytic alkylation of phenol with alcohols by means of a vapor-phase reaction is well known. A large number of related papers have been reported. Enomoto *et al.* have studied the alkylation at the *meta* position of phenol, using a condensed phosphoric acid-Kieselguhr[1] and Al_2O_3–SiO_2[2] as catalysts. Ogata *et al.* have reported the alkylation of phenol with various types of alcohol by means of vapor-phase reactions.[3] The alkylation over solid acidic catalysts is considered to proceed *via* phenyl ether as the intermediate.

It was found in our previous work that the selective methylation at the *ortho* position of phenol over the ZnO–Fe_2O_3 catalyst proceeded by means of a reaction between the *ortho* position of the phenoxide surface species and the methyl cation which is formed on the surface of the catalyst.[4] In this paper, we wish to report the results of the selective alkylation of phenol with various alcohols over the ZnO–Fe_2O_3 catalyst.

Experimental

Materials. The phenol, ethanol, 1-propanol, 2-propanol, and *t*-butyl alcohol were also of an analytical reagent grade. These alcohols were used after one distillation.

Catalyst. The catalyst was prepared as follows: after the dissolution of 1 mol of ferric nitrate and 1 mol of zinc nitrate in 2.2 l of water, a 14% aqueous ammonium solution was added to the solution until it gave a pH value of 6.85. The coprecipitate was washed several times with water, dried at 150 °C in an oven, calcined in air at 400 °C for 3 hr, and sieved to 12–14-mesh-size particles.[5]

Acidic and Basic Properties of the Catalyst. As the catalyst was colored, the acidic and basic properties were measured by means of gas chromatography, as was illustrated in a previous work.[4] The acidity and the basicity were defined as the saturated amounts of the adsorption of pyridine and phenol respectively.

Reaction Apparatus and Conditions. A conventional flow-type reaction apparatus (reactor : Pyrex glass, i.d. 18 mm) was used. A mixture of 1 mol of phenol and 5 mol of alcohol was introduced into the vaporizer; the reaction vapors were carried by nitrogen gas onto the catalyst bed. The partial pressures of phenol, alcohol, and nitrogen gas in the reaction system was 0.058 atm 0.288 atm, and 0.654 atm respectively. The time factor, W/F, was 53.3 g-cat. h/mol-feed. The vaporizer was maintained at about 300 °C, and the temperature of the catalyst bed was controlled at 350 °C.

Analysis of Products. The reaction products were identified by means of infrared, NMR, and mass spectrometry. The content of each component was quantitatively determined by gas chromatography (column: active carbon, Silicon DC 550, and Porapak Q).

Results and Discussion

The catalyst possesses the following properties: the surface area is 26.6 m^2/g, the pore volume is 0.094 ml/g, and the component is analyzed as ZnO–$ZnFe_2O_4$ by X-ray analysis (Fe-Kα radiation). Moreover, the acidic and the basic properties of the catalyst are shown in Fig. 1. Figure 1 shows that: (1) the acidity and the basicity are 91.3 μmol/g-cat. and 98.0 μ mol/g-cat. respectively, (2) the amounts of the adsorption of pyridine on the catalyst after the saturated adsorption of phenol are 3.8 μ mol/g-cat., and (3) the amounts of the adsorption of pyridine decrease from 91.3 μmol/g-cat. to 3.8 μmol/g-cat. with an increase in the amounts of of the pre-adsorbed phenol.

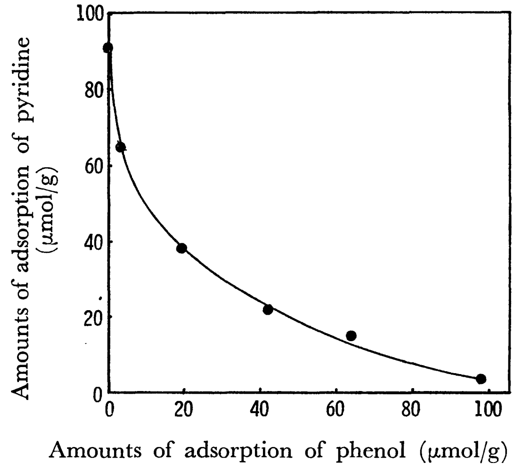


Fig. 1. Acidic and basic properties of the ZnO-Fe_2O_3 catalyst.

From these results, it may be considered that the adsorbed phenol lies on both the acid site and the base site. This seems to mean that a dissociative adsorption of phenol takes place on the catalyst.[4] The products of the reaction between phenol and various alcohols are shown in Table 1. The reaction may be divided into the alkylation of phenol and the decomposition of alcohols.

Alkylation of Phenol: The alkylation of phenol over such a solid acidic catalyst as alumina is said to proceed by means of the rearrangement of alkyl phenyl ether.[2] The ratio of alkylphenol to alkyl phenyl ether in the reaction products depends on the structure of the alcohol.[6] However, the alkylation of phenol over the present catalyst proceeds selectively at the *ortho* position even with various alcohols, as is shown in Table 1. Ogata *et al.* reported that phenol was not only alkylated by the rearrangement of alkyl phenyl ether, but also by the direct nuclear alkylation.[3] The present catalyst

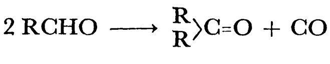
Table 1. Products by the reaction between phenol and various types of alcohols

Alcohol	Ethanol	1-Propanol	2-Propanol	*t*-Butyl alcohol
Conversion of phenol (mol %)	33.1	23.9	12.0	trace
Yields of *o*-alkylphenol (mol %)	26.4	20.2	11.4	trace
Conversion of alc. (mol %)	100	100	100	100
Selectivity (%)				
Acetone	100	—	93.1	—
C_4H_7-CO-CH_3	—	—	1.9	—
4-me-3-Pentene-2-one	—	—	4.8	—
Pentan-3-one	—	86.0	—	—
Hexan-3-one	—	14.0	—	—
iso-Butylene	—	—	—	100
Composition of gaseous products (mol %)				
Carbon dioxide	16.8	18.5	—	—
Hydrogen	78.7	77.1	100	—
Carbon monoxide	4.5	4.5	—	—

can, therefore, be considered to catalyze the nuclear alkylation of phenol directly without the rearrangement of alkyl phenyl ether. For the nuclear alkylation, phenol must be dissociated on the surface of the catalyst. In the previous work, it was described that selective methylation at the *ortho* position of phenol was carried out by the reaction between the phenoxide surface species and the methyl cation.[4] If this mechanism is applied in this study, the alkylation of phenol with various alcohols may also be effected to take place at the *ortho* position. The high selectivity for the alkylation at the *ortho* position of phenol may be concluded to be caused by the dissociative adsorption of phenol on the acid site and the base site of the present catalyst.

Decomposition of Alcohols: The ethanol and 1-propanol decomposed to form gaseous products and ketones. The gaseous products from primary alcohols were composed of 17% of CO_2, 78% of H_2, and 4.5% of CO. From these facts, the path of the decomposition of primary alcohols may be considered to be as follows;

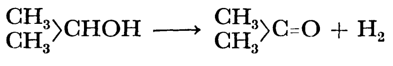
$$2\,RCH_2OH \longrightarrow 2\,RCHO + 2\,H_2 \tag{1}$$



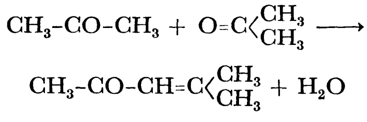
$$2\,RCHO \longrightarrow {}^{R}_{R}\!\!>\!C{=}O + CO + H_2 \tag{2}$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{3}$$

where R denotes a methyl or ethyl group. 2-propanol decomposed to form hydrogen, acetone, and small amounts of unsaturated ketone (C_4H_7–CO–CH_3). From these facts, the reaction may be considered to proceed as follows;



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CHOH \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C{=}O + H_2 \tag{4}$$



$$CH_3\text{-}CO\text{-}CH_3 + O{=}C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} \longrightarrow CH_3\text{-}CO\text{-}CH{=}C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} + H_2O \tag{5}$$

t-butyl alcohol decomposed to form *iso*-butylene and water by dehydration, which is said to proceed in an acidic medium.

References

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