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# Methylation of Phenol over Metallic Oxides

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Methylation took place only at *ortho* position of phenol under an atmospheric pressure at 350°C when the reaction was carried out over an MO–$Fe_2O_3$ catalyst containing Cu, Mg, Ca, Ba, Zn, Mn, Co, or Ni each as M. The aromatic fraction in liquid products was only *o*-cresol and 2,6-xylenol and products substituted at *para* and *meta* positions could not be obtained. However, gasification of methanol took place simultaneously as a side reaction. From the relation between methylation and gasification, the catalytic activity was found to be effective in the order Cu>Zn>Ba>Ca>Co>Mn>Mg>Ni. Deactivation of these catalysts was observed before the reaction reaches a steady state. The thermogravimetric curve of the used catalyst was measured. From thermal analysis the reduction of the catalyst seems to be a cause of deactivation in addition to deposition of carbonaceous materials onto the catalyst surface. The used catalysts were reclaimed through the process of Scheme 1.

The catalytic alkylation of phenols by vapor phase reaction with alcohols is well known and is used for preparation of alkyl phenols.[1-3] However, because of its low selectivity for a desired alkyl phenol, application of the reaction is limited.

Since poly(2,6-dimethyl)phenylene oxide, the so-called PPO resin, has been introduced as a new thermo-resistant polymer,[4-5] the synthesis of its monomer, 2,6-xylenol, has attracted special attention in industry. A large number of related patents and papers have appeared on synthetic methods using vapor phase or liquid phase reaction. It has been reported that the vapor phase reaction of phenol with methanol over magnesium oxide gives 2,6-xylenol in an exellent yield.[6] A vapor phase synthetic method using $Ce_2O_3$-MnO-MgO as a catalyst has also been reported.[7] This demonstrates that magnesium oxide is most favorable in the synthesis of 2,6-xylenol as compared

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2) N. M. Cullinane and S. J. Chard, *J. Chem. Soc.*, **1945**, 821.
3) Y. Ogata and M. Itoh, *Kogyo Kagaku Zasshi*, **70**, 911 (1967).
4) A. S. Hay, G. F. Endres, and J. W. Eustance, *J. Amer. Chem. Soc.*, **81**, 6335 (1959).
5) A. S. Hay, *J. Polymer Sci.*, **58**, 581 (1962).
6) General Electric Company, U. S. 3446856 (1964).
7) S. Enomoto and M. Inoue, An abstract presented in the 23th Annual Meeting of the Catalysis Society of Japan, Sendai, 3, (1968).

with other catalysts which are used in the methylation of phenol.

We found that methylation occurs only at *ortho* position of phenol under an atmospheric pressure at 350°C when the reaction is carried out over an MO-$Fe_2O_3$ catalyst containing Cu, Mg, Ca, Ba, Zn, Co, Mn, or Ni each as M. This synthetic method of 2,6-xylenol using these types of catalysts is not found in literature. It is, therefore, of particular interest to selectively synthesize 2,6-xylenol without using magnesium oxide as the main component of catalyst. We wish to report on the methylation of phenol over a new type of catalyst.

## Experimental

*Materials.* Phenol and methanol were of analytical reagent grade. They were free from any impurities as ascertained by gas chromatography. Cupric, magnesium, calcium, barium, zinc, manganese, nickel, cobalt, and ferric nitrate were also analytical reagent grade.

*Preparation of Catalysts.* The catalysts were prepared as follows: 1) After dissolution of 0.2 mol of ferric nitrate and 0.1 mol of magnesium, calcium, barium, or zinc nitrate in water, 14% aqueous ammonium solution was added to the solution until it gave a pH of 6.4 at room temperature. 2) After dissolution of 0.2 moles of ferric nitrate and 0.1 mol of cupric, manganeses, nickel or cobalt nitrate in water, 3N aqueous sodium hydroxide solution was added to the solution until it gave a pH of 9.6 at room temperature. The coprecipitate consisting of an individual metallic hydroxide and ferric hydroxide was washed several times with water and calcined in an electric furnace at 400°C for 3 hr with air pumped into the container. These catalysts were crushed and sieved to 12—14 mesh size particles.

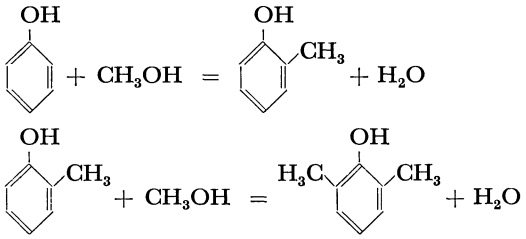
*Thermal Analysis of the Used Catalysts.* A Rigaku Denki "Thermoflex 8002D" was employed in the differential thermogravimetric analysis.

*Analysis of Products.* Carbon dioxide in gaseous products was determined by means of the Hempel gas analytical method. Other gases were identified by comparing their respective retention time on the gas chromatogram against authentic samples, after which they were determined quantitatively by gas chromatography (Column: molecular sieve 13X, carrier gas: Ar gas). Liquid products were identified by gas chromatography and infrared spectrometry. Respective quantitative analysis was performed by gas chromatography (Column: Silicone DC 550 at 170°C and Porapak Q at 110°C, carrier gas: He gas).

*Apparatus.* A Pyrex glass tubular reactor (500 mm length, 20 mm o.d., 18 mm i.d.) was connected with a micro pump which feeds reactants, vertically supported and externally heated in an electric furnace. A vaporizer above the catalyst bed was surrounded by an electric heater and maintained at temperatures 250—280°C. The reactant vapors carried with nitrogen gas were led over the catalyst bed through the vaporizer. The reaction temperature was measured with an IC thermocouple placed in the middle of the catalyst bed. The product vapors were led through an air-cooled condenser and two dry ice traps, and non-condensable products were determined with a wet gas meter.

## Results and Discussion

Phenol is methylated consecutively to 2,6-xylenol *via* *o*-cresol by the following processes.




At a high temperature, however, it is decomposed to form benzene, toluene, and xylene. To avoid this, the optimal reaction condition was selected as follows. One mole of phenol is reacted with 10 moles of methanol at 350°C. Partial pressure of nitrogen gas carrier is 0.38 atom. The contact time is 1.6 sec at 350°C.

We see from Table 1a that phenol is selectively methylated at *ortho* position. Even with a large

Table 1a. Reaction products over MO-$Fe_2O_3$ catalyst

| M of MO-$Fe_2O_3$ | Cu | Mg | Ca | Ba | Zn | Mn | Co | Ni[a] |
|---|---|---|---|---|---|---|---|---|
| Phenol converted, mol % | 95.3 | 8.8 | 68.7 | 82.5 | 88.4 | 24.0 | 63.9 | 67.5 |
| Selectivity, %[b] | | | | | | | | |
| *o*-Cresol | 41.0 | 75.3 | 79.3 | 64.3 | 43.5 | 83.9 | 82.6 | 53.2 |
| 2,6-Xylenol | 59.0 | 24.7 | 20.3 | 35.6 | 56.5 | 13.1 | 17.3 | 18.6 |
| Methanol converted, mol % | 42.3 | 5.1 | 23.1 | 28.7 | 66.5 | 2.2 | 23.8 | 98.3 |
| Selectivity, %[c] | | | | | | | | |
| Methylation | 31.5 | 22.1 | 41.9 | 38.7 | 21.0 | 100 | 32.5 | 6.6 |
| Gasification | 68.5 | 77.9 | 58.0 | 61.3 | 79.0 | — | 67.5 | 93.3 |

a) Selectivity for benzene, toluene, xylene, and carbonization are 12.4, 5.0, 1.0, and 9.8, respectively.
b) Given by (moles of *o*-cresol or 2,6-xylenol per moles of phenol converted).
c) Given by (moles of methyl group in products or gaseous products per moles of methanol converted).

Table 1b. Compositions of gaseous products over MO-$Fe_2O_3$ catalysts

| M of MO-$Fe_2O_3$ | Cu | Mg | Ca | Ba | Zn | Mn | Co | Ni |
|---|---|---|---|---|---|---|---|---|
| Carbon dioxide, mol % | 17.5 | 17.6 | 16.1 | 17.3 | 18.2 | — | 16.9 | 17.8 |
| Hydrogen, mol % | 53.5 | 49.1 | 37.4 | 39.0 | 64.2 | — | 51.7 | 64.4 |
| Methane, mol % | 21.7 | 27.0 | 37.0 | 35.3 | 7.9 | — | 21.4 | 12.6 |
| Carbon monoxide, mol % | 7.3 | 6.3 | 9.5 | 8.4 | 9.7 | — | 10.1 | 5.2 |

Table 2. Surface area of fresh and used catalysts

| M of $MO-Fe_2O_3$ | Cu | Mg | Ca | Ba | Zn | Mn | Co | Ni |
|---|---|---|---|---|---|---|---|---|
| Fresh catalyst, $m^2/g$ | 74.7 | 4.4 | 25.3 | 20.9 | 24.2 | 38.0 | 74.3 | 113.4 |
| Used catalyst, $m^2/g$ | 22.1 | 5.2 | 21.8 | 18.5 | 17.0 | 25.1 | 42.4 | 76.9 |

excess of methanol, the aromatic fraction in liquid products is only *o*-cresol and 2,6-xylenol except for the case in which $NiO-Fe_2O_3$ catalyst is used. In contrast, methanol reacts through two simultaneous pathways, the methylation of phenol and the gasification of methanol itself. Using gaseous components in Table 1b, the gasification of methanol can be demonstrated by

$$CH_3OH = CO + 2H_2 \quad (1)$$

$$CO + 3H_2 = CH_4 + H_2O \quad (2)$$

$$CO + H_2O = CO_2 + H_2 \quad (3)$$

These pathways can be expected from the fact that the $Fe_2O_3$ catalyst promotes reactions (2) and (3). Thus, this type of catalyst promotes the selective methylation at *ortho* position of phenol and simultaneously the gasification of methanol. Effectiveness of these catalysts should be discussed from the relation between the main reaction and the undesired side reaction. Figure 1 shows the relation between the methylation and gasification. The upper-right region in Fig. 1 denotes where the methylation only takes place and lower-left region denotes where the gasification only takes place. Thus, it can be said that these catalysts are effective in the order Cu>Zn>Ba>Ca>Co>Mn>Mg>Ni.

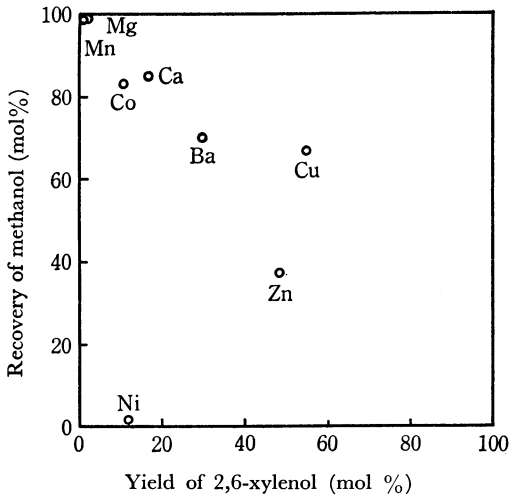



Fig. 1. Relation between methylation and gasification.

Tables 1a and 1b show the data which were obtained around six or seven hours after the commencement of the reaction. However, deactivation of the catalysts is observed before the reaction reaches a steady state. Figure 2 shows the course of deactivation.

The surface area and the differential thermogravimetric curve of the used catalysts were determined in order to estimate the degree of deactivation of catalyst which is said to depend on decrease of surface area caused by sintering of catalyst and also on the contamination of active sites by carbon deposition. The

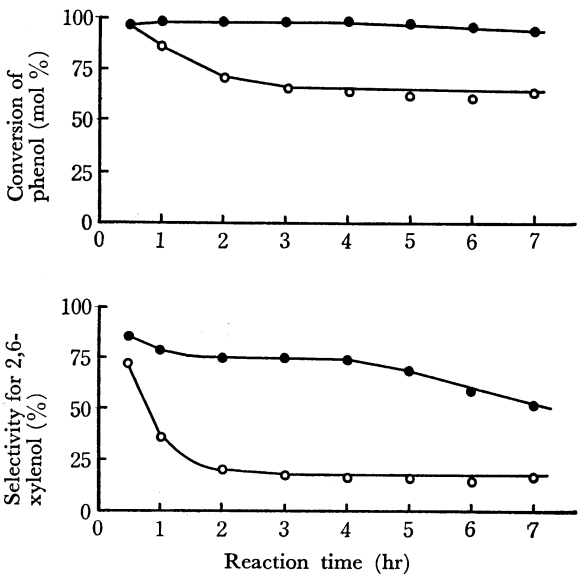



Fig. 2. Activity *vs.* reaction time.
—●— $CuO-Fe_2O_3$, —○— $CoO-Fe_2O_3$

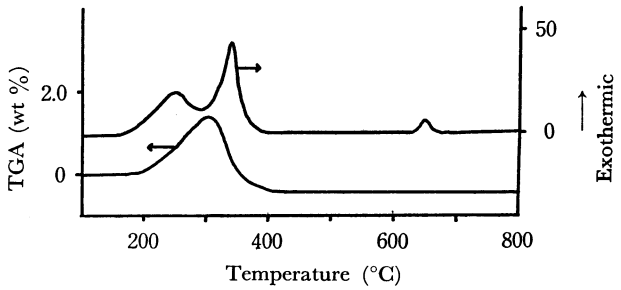



Fig. 3. A typical differential thermogravimetric curve.
Conditions: Heating rate 10°C/min, TGA sens. 5 mg DTA sens., ±100 μV, Atmosphere, air.

Table 3a. Free energies of formation[8]

| Oxide | $\Delta G^0_f$ (kcal/mol) | Oxide | $\Delta G^0_f$ (kcal/mol) |
|---|---|---|---|
| CuO | −30.4 | MnO | −86.8 |
| MgO | −136.13 | CoO | −51.0 |
| CaO | −144.4 | NiO | −51.7 |
| BaO | −126.3 | $Fe_2O_3$ | −177.1 |
| ZnO | −76.05 | $Fe_3O_4$ | −242.4 |

Table 3b. Molar enthalpies of formation at 970° K

| Process | $\Delta H_{970}$ kcal/mol | Ref. |
|---|---|---|
| $CuO + Fe_2O_3 = CuFe_2O_4$ (I) | +5.05 | (9) |
| $MgO + Fe_2O_3 = MgFe_2O_4$ (0.9 I) | −4.43 | (9) |
| $ZnO+Fe_2O_3=ZnFe_2O_4$ (N) | −2.67 | (9) |
| $MnO+Fe_2O_3=MnFe_2O_4$ (0.2 I) | −5.0 | (10) |
| $CoO+Fe_2O_3=CoFe_2O_4$ (I) | −5.89 | (9) |
| $NiO+Fe_2O_3=NiFe_2O_4$ (I) | −1.22 | (9) |

N—normal spinel M $(Fe_2)O_4$
I—inverse spinel Fe $(MFe)O_4$

TABLE 4. RESULTS OF DIFFERENTIAL THERMOGRAVIMETRIC ANALYSIS OF THE USED CATALYST

| M of MO-$Fe_2O_3$ | Cu | Mg | Ca | Ba | Zn | Mn | Co | Ni |
|---|---|---|---|---|---|---|---|---|
| Wt. increased, wt % | 6.11 | 0.67 | 1.93 | 0.83 | 0.95 | 1.70 | 0.41 | 2.27 |
| DTA(I), °C | 233 | 237 | 217 | 222 | 222 | 240 | 232 | 334 |
| Wt. decreased, wt % | 2.00 | trace | 1.81 | 0.47 | 1.18 | 2.98 | 0.85 | 16.25 |
| DTA (II), °C | 334 | 270 | 326 | 310 | 326 | 375 | 276 | 395 |
| DTA (III), °C | — | 477 | 495 | 484 | 645 | 560 | 665[a)] | 530[a)] |

a) Measured from coprecipitates of hydroxides.

surface area of the fresh and the used catalysts is shown in Table 2 and a typical differential thermogravimetric curve is shown in Fig. 3.

Figure 3 is divided into three parts, (I) exothermic with a weight increase, (II) exothermic with a weight decrease, and (III) exothermic without a weight change. (I) is due to the oxidation of the used catalyst which has been reduced during the reaction. As would be expected from molar free energies in Table 3a,[8] hematite in the fresh catalyst is reduced to magnetite. This was confirmed through the thermal analysis of the mixture of MO and $Fe_3O_4$. (II) is due to the combustion of carbonaceous materials which deposited during the course of reaction. (III) is due to the following solid reaction.

$$MO + Fe_2O_3 = M(Fe_2)O_4$$
$$MO + Fe_2O_3 = Fe(MFe)O_4$$

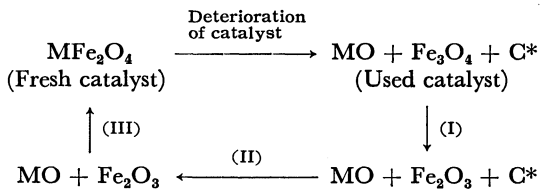
It is expected from molar enthalpies of formation in Table 3b that (III) is exothermic except for CuO-$Fe_2O_3$.[9-10] The solid reaction was confirmed by means of X-ray diffractometry before and after the exothermic peak. Behaviors of the used catalyst in differential thermogravimetric analysis can be summerized as follows.

The result of thermal analysis is shown in Table 4.

Here, the degree of reduction in the case all catalysts except CuO–$Fe_2O_3$ does not exceed the calculated value which is given by the following expression.

$$[1 - (3MO, 2Fe_3O_4/3MO\text{-}Fe_2O_3)] \times 100$$

However, in the case of CuO-$Fe_2O_3$, it exceeds the calculated value (2.24%) because the reduction takes place not only in hematite, but also in cupric oxide. Thus, the reduction of the catalyst would give rise to the deactivation of the catalyst besides the decrease of the surface area and deposition of carbonaceous materials onto the catalyst surface. Thermal analysis was carried out in order to discuss deactivation of the catalyst, and Scheme 1 can be regarded as a process for the reclamation of the used catalyst.




Scheme 1

C* shows carbonaceous materials.

A large number of studies, by the reaction of phenol with methanol over magnesium oxide or modified magnesium oxides, are mainly concerned with the ring substitutive reaction of phenol. However, this paper deals with not only the ring substitutive reaction, but also the thermal analysis of the used catalyst.

Thus, we may conclude that the present catalyst gives an excellent catalytic activity for selective methylation at *ortho* position of phenol and its activity is effective in the order Cu>Zn>Ba>Ca>Co>Mn>Mg>Ni, and the used catalyst is reclaimed through the process of Scheme 1.

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