

# Benzene Hydroxylation to Phenol Catalyzed by Transition Metals Supported on MCM-41 and Activated Carbon

Jung-Sik Choi, Tae-Hwan Kim<sup>\*†</sup>, M. B. Saidutta<sup>\*\*</sup>, Jae-Suk Sung<sup>\*</sup>, Kweon-Il Kim<sup>\*</sup>,  
R. V. Jasra<sup>\*\*\*</sup>, Sun-Dal Song<sup>\*\*\*\*</sup>, and Young-Woo Rhee

*Department of Chemical Engineering, Chungnam National University, Daejeon, Korea*

*\*Korea Institute of Energy Research (KIER), Daejeon, Korea*

*\*\*Department of Chemical Engineering, National Institute of Technology Karnataka, Surathkal, Mangalore-575 025, India*

*\*\*\*Central Salt & Marine Chemical Research Institute (CSMCRI), Bhavnagar, 364 002, India*

*\*\*\*\*Department of Physics, Hanseo University, Chungnam, Korea*

Received June 2, 2003; Accepted November 3, 2003

---

**Abstract:** The direct conversion of benzene to phenol by hydroxylation with hydrogen peroxide was carried out over various transition metals impregnated on MCM-41 and activated carbon. Copper-, iron-, and vanadium-impregnated on activated carbon gave better yields of phenol when compared to the corresponding reactions using cobalt-, nickel-, manganese-, and titanium-impregnated catalysts. Comparison of the MCM-41- and activated carbon-supported catalysts showed that activated carbon-supported catalysts gave a higher yield of phenol than did the MCM-41-supported catalysts. The activity of the transition metals supported on activated carbon in the production of phenol was  $V > Fe > Cu$ ; the corresponding activity of the transition metals supported on MCM-41 was  $Cu > Fe > V$ . In addition to the role of transition metals in catalyzing the hydroxylation reaction, the hydrophobic nature of the activated carbon surface seems to enhance the performance of these catalysts relative to the MCM-41-supported catalysts.

**Keywords:** benzene hydroxylation, phenol, MCM-41, activated carbon

---

## Introduction

Phenol is a starting material for the preparation of numerous intermediates and finished products. About 90% of the worldwide production of phenol occurs by the Hock process (cumene oxidation) and the rest by the toluene oxidation process. In the Hock process, for every mole of phenol produced, one mole of acetone is also produced. Even though acetone is a good solvent, its market demand is not as high as that for phenol. Both the commercial processes for phenol production are multistep processes and, thereby, they are inherently unclean. Therefore, there is a need for a cleaner method for the production of phenol that is both economically and environmentally viable. There is great interest amongst

researchers to develop a new method for the synthesis of phenol that occurs in a one-step process. Much work is being carried out to develop a suitable catalyst for the direct hydroxylation of benzene to phenol.

Processes for the direct conversion of benzene to phenol can be categorized broadly into vapor-phase and liquid-phase oxidation processes.  $N_2O$ , oxygen, and air have been used as oxidants in the vapor-phase oxidation processes, whereas hydrogen peroxide, oxygen, and air have been used as oxidants in the liquid-phase oxidation processes.

Gas-phase oxidation of benzene to phenol by nitrous oxide has been studied over various supported transition metal oxide catalysts [1], ZSM-5-type zeolite catalysts [2-6], Fe-modified TS-1 catalysts [7], and Fe-silicalite catalysts [8]. Studies have been conducted using oxygen as an oxidant in the gas-phase oxidation of benzene to phenol over Cu salts in the presence of ascorbic acid as a reductant [9]. Palladium and hetero-polyacids [10], Cu-

---

<sup>†</sup> To whom all correspondence should be addressed.  
(e-mail: thkim@kier.re.kr)

supported ZSM-5 catalysts [11], and silica-supported vanadium oxide catalysts modified with palladium or platinum [12] also have been investigated.

Liquid-phase oxidation of benzene to phenol using oxygen as an oxidant has been studied over nickel-containing macrocyclic dioxopentaamines [13]. Cu-Zeolites [14], precious metals supported on silica and modified with vanadium oxide [15], Cu-supported mesoporous silicates and aluminosilicates [16], heteropolyacids encapsulated in MCM-41 and VPI-5 [17], co-precipitated CuO-Al<sub>2</sub>O<sub>3</sub> catalysts [18], platinum/supported on silica and promoted by vanadium/iron/lanthanum/yttrium [19], and vanadium supported on alumina [20] also have been investigated.

The liquid-phase oxidation of benzene to phenol using hydrogen peroxide as an oxidant has been studied over  $\alpha$ -pyrrolidone-bridged mixed-valent tetranuclear platinum complexes [21], and also over selectively site-substituted heteropolytungstates [22]. Polymer-bound vanadyl acetyl acetonate [23], TS-1 molecular sieves [24,25], a water-soluble catalytic system based on iron complexes of polyethylene oxide functionalized by  $\beta$ -cyclodextrin [26], vanadium-substituted polyoxometalate catalysts [27], vanadium-containing MCM-41 and MCM-48 catalysts [28], Ti-MCM-41 catalysts [29], amorphous microporous mixed oxides containing Fe, V, Cr, and Cu [30], and vanadium supported on alumina [20] also have been investigated for this reaction.

Of all the catalysts that have been studied so far, ZSM-5-based catalysts have been found to have superior performance relative to the other catalytic materials for the vapor-phase oxidation of benzene to phenol. In the liquid-phase oxidation, TS-1 and Ti-MCM-41 catalysts have the best properties relative to other catalytic materials that have been tested.

Mesoporous silica materials, like MCM-41, possess both well-ordered and long-range pore structures and their surface properties can also be modified to enhance their catalytic activity; these characteristics have led to the increased use of these materials as catalysts or supports. There have been reports [29,31] on the effects of surface modification, its influence on surface hydrophobicity/hydrophilicity, and its effect on the catalytic selectivity towards phenol in the hydroxylation of benzene on Ti-MCM-41 catalysts.

Activated carbon materials, which have large surface areas, are used as adsorbents, catalysts, and catalyst supports. The chemical surface functionality of activated carbon is due to the oxygen-containing chemical groups on the surface, which render the surfaces as either acidic, basic, or neutral. Activated carbons also have favorable hydrophobicity/hydrophilicity, which makes them suitable for the benzene hydroxylation.

Transition metals are used widely as catalytically active materials for the oxidation/hydroxylation of various aro-

matic compounds. To the best of our knowledge, there have been no reports on the use of activated carbon supported catalysts for the hydroxylation reaction.

Taking these factors into consideration, we have prepared catalysts containing various transition metals impregnated on MCM-41 and activated carbon and tested their activities toward the hydroxylation of benzene to phenol using hydrogen peroxide.

## Experimental

### Synthesis of MCM-41

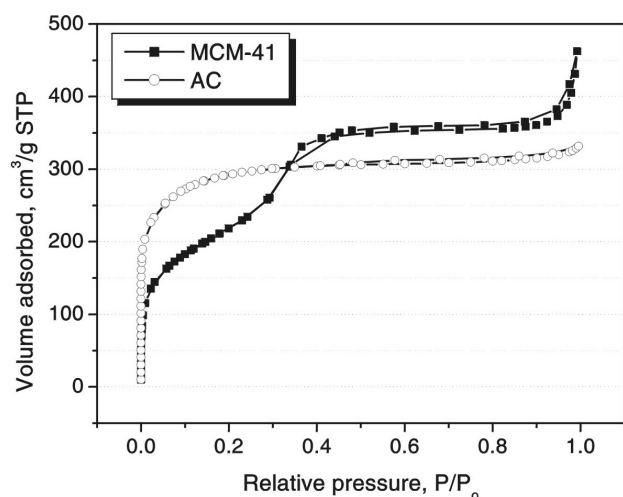
MCM-41 was prepared by the hydrothermal method [32]. The chemicals used to synthesize MCM-41 were silica (Aldrich), cetyltrimethylammonium bromide [CTABr, C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>3</sub>NBr, Aldrich] as the templating agent, sodium silicate solution containing 27% SiO<sub>2</sub> and 14% NaOH (Aldrich), and distilled water. The gel that was obtained by mixing the reactants had the molar composition 4SiO<sub>2</sub>:1Na<sub>2</sub>O:1CTABr:200H<sub>2</sub>O. The gel so obtained was processed for 3 days in a teflon-lined autoclave at 100°C and the pH (9.5~10) was adjusted once a day using acetic acid. The synthesized MCM-41 was washed with 2% HCl: EtOH solution, filtered, dried at 373 K overnight, and, subsequently, calcined at 823 K for 4 h. The heating rate was 2.5°C/min. Activated carbon (AC, Samchully Activated Carbon Co, Ltd.), which was also used as a catalyst support, was obtained from a commercial source.

### Preparation of Catalysts

All the impregnated catalysts were prepared in a rotary evaporator using the appropriate transition metal salts. The quantity of transition metal impregnated was 0.5 wt%. The quantity of copper loaded was 0.5, 1.0, 2.0, and 5.0 wt% on both MCM-41 and activated carbon. The MCM-41-supported catalysts were dried and calcined in a furnace at 550°C for 4 h under an atmosphere of air. AC-supported catalysts were calcined under a nitrogen atmosphere at 550°C [14] for 4 h.

### Catalysts Characterization

XRD data for all Cu-impregnated catalysts were obtained on a Rigaku instrument (D/Max2000-Ultima plus; X-ray radiation, CuK  $\alpha$ ). Nitrogen adsorption-desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 apparatus. From these studies, we obtained the BET surface area, pore size distribution, and pore volume. The amount of benzene and methanol adsorbed were measured gravimetrically at 60°C using a magnetic suspension balance (MSB; Rubotherm, Germany). TEM analysis (JEOL, JEM-2010) of synthesized MCM-41 was undertaken to determine its ordered long-range pore



**Figure 1.**  $N_2$  adsorption-desorption isotherms of MCM-41 and AC.

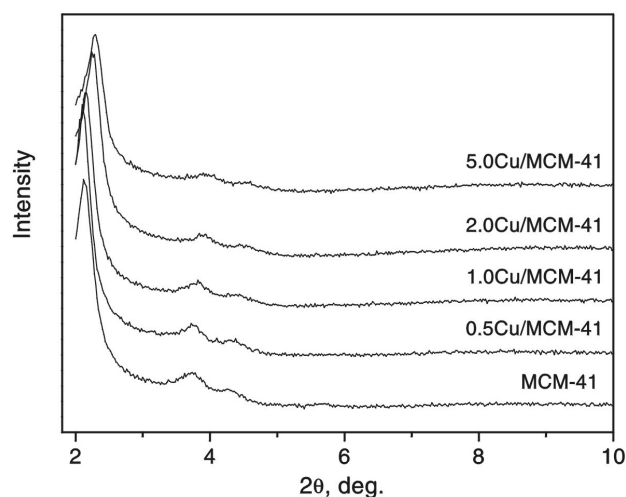
structure. Cu-impregnated AC catalysts were analyzed by FE-SEM (LEO-1530FE).

### Benzene Hydroxylation

Benzene hydroxylation reactions were carried out in a stainless-steel reactor; the reactor contents were mixed thoroughly using a magnetic stirrer. Reactions were carried out at a temperature of 65°C. Acetone was used as the solvent and  $H_2O_2$  (30 wt%) as the oxidant. The molar ratio of reactants, benzene: $H_2O_2$ :solvent, was 1:3:8. In all of the experimental runs, 0.1 g of catalyst was used. The reaction time was 5 h. The products were analyzed by HPLC (Waters 2690) using a reverse-phase C18 column, a UV detector at monitoring 254 nm, and a mobile phase consisting of water and acetonitrile (42:58, v/v).

## Results and Discussion

Nitrogen adsorption-desorption isotherms of MCM-41



**Figure 2.** The XRD patterns of MCM-41-supported catalysts.

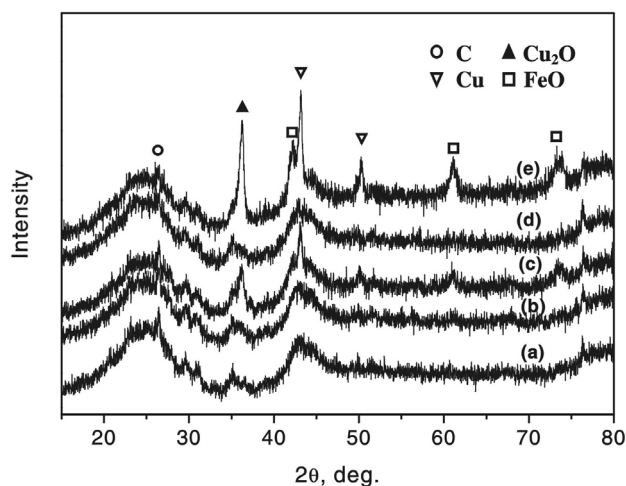
and activated carbon are presented in Figure 1. The BET surface area, pore volume, and pore size of all the catalysts used in this study are given in Table 1. Nitrogen adsorption experiments showed a typical type IV isotherm for MCM-41 catalysts and a type I isotherm for activated carbon catalysts. The desorption isotherms for MCM-41 showed hysteresis, which indicates the presence of mesopores, whereas activated carbon possesses mostly micropores. Even though MCM-41 catalysts have smaller surface areas relative to those of the activated carbon catalysts, their pore volumes were comparable, indicating the presence of large mesopore volumes in the MCM-41 catalysts.

The XRD patterns of various copper-impregnated MCM-41 catalysts are given in Figure 2. The XRD patterns indicate the presence of well-ordered hexagonal pore structures in the MCM-41 catalysts. This figure also shows that the treatment during the impregnation of copper and the calcination steps do not lead to the destruction of this pore structure. The XRD patterns of activated carbon-

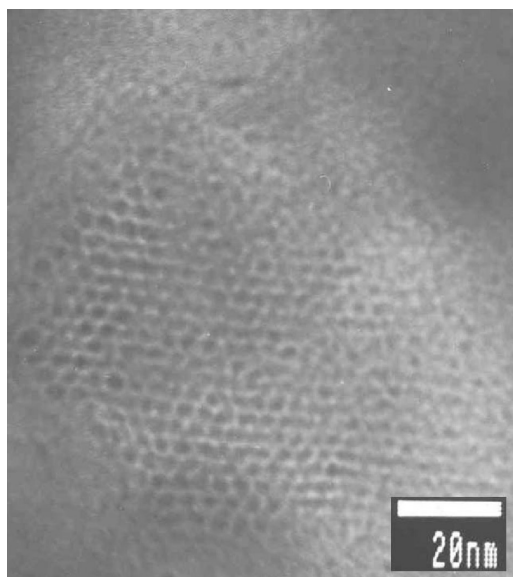
**Table 1.** BET Surface Area, Pore Volume, and Pore Size of All Catalysts Used in This Study

| Support               | Metal, wt% | BET surface area, $m^2/g$ | Micropore volume, $cm^3/g$ | Median pore radius, $\text{\AA}^*$ |
|-----------------------|------------|---------------------------|----------------------------|------------------------------------|
| MCM-41                | 0.5Cu      | 656.7                     | 0.4301                     | 5.7                                |
|                       | 1.0 Cu     | 638.9                     | 0.4278                     | 5.8                                |
|                       | 2.0 Cu     | 634.6                     | 0.3933                     | 6.3                                |
|                       | 5.0 Cu     | 612.3                     | 0.3745                     | 6.3                                |
| Activated Carbon (AC) | 0.5 Cu     | 1181.7                    | 0.5031                     | 3.0                                |
|                       | 1.0 Cu     | 1119.5                    | 0.4659                     | 2.8                                |
|                       | 2.0 Cu     | 1057.3                    | 0.4533                     | 2.8                                |
|                       | 5.0 Cu     | 1026.9                    | 0.4278                     | 2.8                                |
| MCM-41                | 0.5Fe      | 733.3                     | 0.4843                     | 6.2                                |
|                       | 0.5V       | 714.5                     | 0.4639                     | 6.2                                |
| Activated Carbon (AC) | 0.5Fe      | 1087.5                    | 0.4638                     | 2.8                                |
|                       | 0.5V       | 1017.4                    | 0.4387                     | 2.7                                |
|                       | 0.5Ni      | 1081.0                    | 0.4508                     | 2.8                                |
|                       | 0.5Mn      | 1103.7                    | 0.4739                     | 2.9                                |
|                       | 0.5Co      | 1101.1                    | 0.4630                     | 2.9                                |
|                       | 0.5Ti      | 708.4                     | 0.3800                     | 2.3                                |

\* Median pore radius was calculated by the Horvath-Kawazoe method.



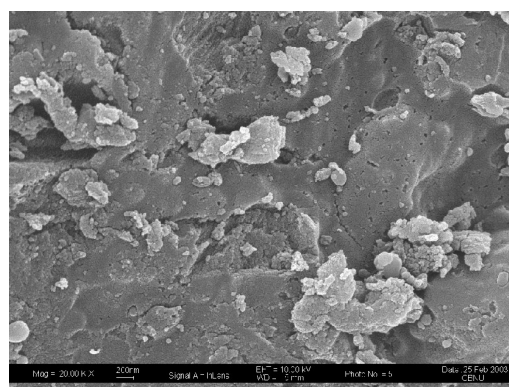
**Figure 3.** The XRD patterns of AC-supported catalysts. (a) AC; (b) 0.5 wt% Cu/AC; (c) 1.0 wt% Cu/AC; (d) 2.0 wt% Cu/AC; (e) 5.0 wt% Cu/AC.



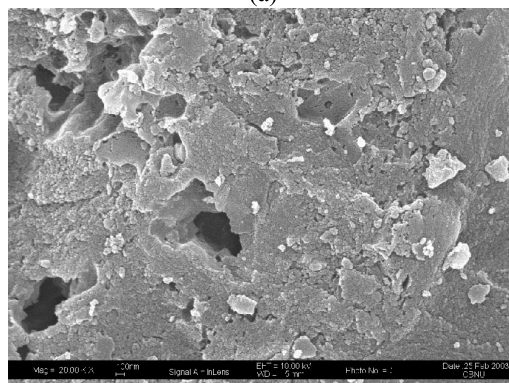
**Figure 4.** TEM image of synthesized MCM-41.

supported copper catalyst, shown in Figure 3, indicate the presence of copper in the form of copper oxide and metallic copper. This observation can be attributed to the fact that the activated carbon catalysts were calcined in the presence of nitrogen at 550°C for 5 h after the impregnation with copper. Because these catalysts were dried at 100°C, to drive out adsorbed moisture prior to their use in reaction studies, part of the impregnated copper might have become oxidized.

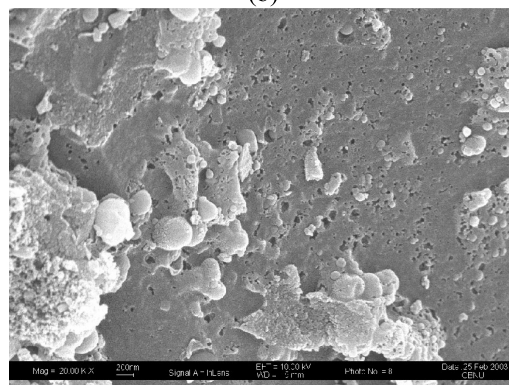
The transmission electron micrograph presented in Figure 4 shows the well-ordered hexagonal structure of the MCM-41 material. The scanning electron micrographs of various copper-impregnated activated carbon catalysts are presented in Figure 5. Agglomeration of copper can be observed on the surface of the activated carbon as the impregnated amount of copper increased from 0.5 to 5.0 wt%.



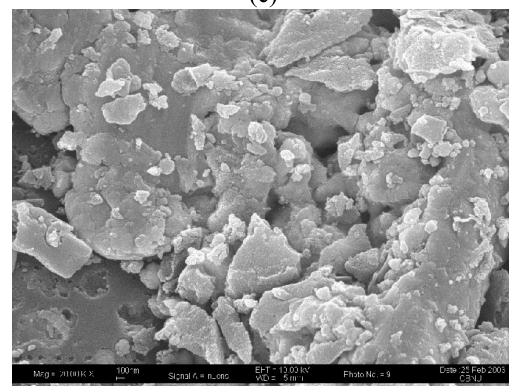
(a)



(b)



(c)



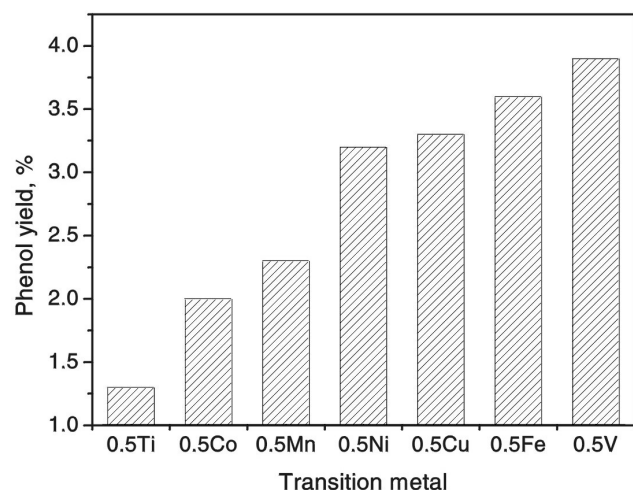
(d)

**Figure 5.** SEM images of AC-supported catalysts. (a) 0.5 wt% Cu/AC; (b) 1.0 wt% Cu/AC; (c) 2.0 wt% Cu/AC; (d) 5.0 wt% Cu/AC

**Table 2.** Hydrophilic/Hydrophobic Properties of Several Catalysts at 100 torr

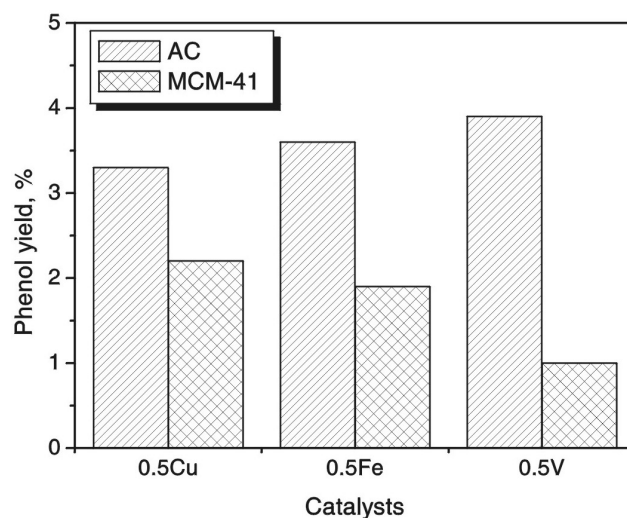
| Support               | Cu, wt% | Benzene (Bz) adsorbed, mmol/g | Methanol (MeOH) adsorbed, mmol/g | $A_{Bz} / A_{MeOH}^*$ |
|-----------------------|---------|-------------------------------|----------------------------------|-----------------------|
| MCM-41                | 0.5     | 2.11134                       | 2.89728                          | 0.72873               |
|                       | 1.0     | 1.76357                       | 2.68578                          | 0.65663               |
|                       | 2.0     | 1.81237                       | 2.53409                          | 0.71520               |
|                       | 5.0     | 1.70108                       | 2.47518                          | 0.68726               |
| Activated Carbon (AC) | 0.5     | 4.60979                       | 3.30093                          | 1.39651               |
|                       | 1.0     | 4.18232                       | 3.34997                          | 1.24846               |
|                       | 2.0     | 4.13119                       | 1.59820                          | 2.58490               |
|                       | 5.0     | 3.98023                       | 1.39324                          | 2.85682               |

\*  $A_{Bz}/A_{MeOH}$  refers to the ratio of the quantity of adsorbed benzene to the quantity of adsorbed methanol.

**Figure 6.** Phenol yield obtained over different transition metal-loaded AC catalysts.

Benzene and methanol adsorption studies were conducted on MCM-41 and activated carbon catalysts to determine the surface hydrophobicity and hydrophilicity of these materials, respectively; the results are presented in Table 2. Adsorption of benzene on activated carbon catalysts was greater than that on MCM-41 catalysts, indicating that the surface, of the activated carbon catalysts are more hydrophobic than are the surfaces of the MCM-41 catalysts. Adsorption of methanol on activated carbon catalysts was lower than that on MCM-41 catalysts, indicating that the surfaces of the activated carbon catalysts are less hydrophilic than are the surfaces of the MCM-41 catalysts.

The benzene hydroxylation using hydrogen peroxide was carried out using catalysts comprising various transition metals (each 0.5 wt%) impregnated on activated carbon. The yields of phenol obtained over these catalysts are shown in Figure 6. The phenol yield is defined as the number of moles of phenol produced per mole of benzene consumed. We observe that the yields vary from 1.3% (on 0.5 wt% Ti impregnated on activated carbon) to 3.9% (on 0.5 wt% vanadium impregnated on activated carbon). Copper-, iron-, and vanadium-impregnated catalysts gave the best results amongst the activated carbon-

**Figure 7.** Comparison of the yield of phenol obtained over different transition metals loaded on AC and MCM-41 catalysts.

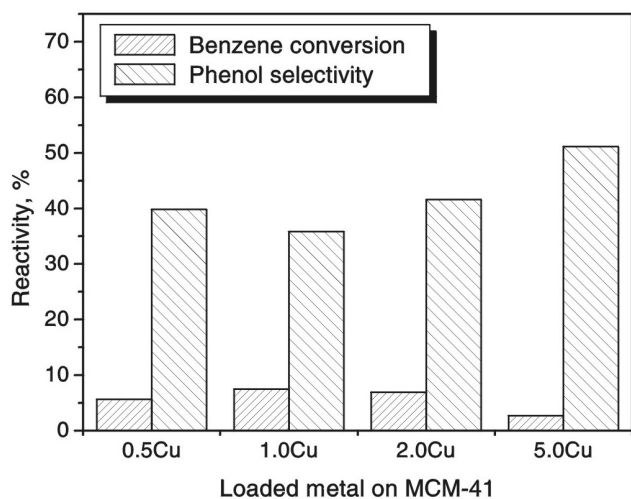
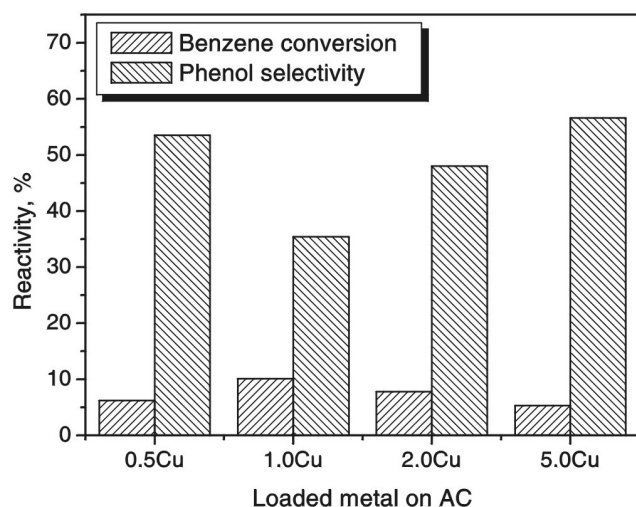
supported catalysts. Copper, iron, and vanadium were chosen to compare of the performance of the activated carbon and MCM-41 supports for the transition metal-impregnated catalysts during benzene hydroxylation. The results are shown in Figure 7. We observe that, in the case of the MCM-41 support, the performance in terms of the yield of phenol increased in the order  $Cu > Fe > V$ . In contrast, in the case of the activated carbon-supported catalysts, the order was  $V > Fe > Cu$ . Copper impregnated on MCM-41 gave twice the yield of phenol relative to that obtained using vanadium impregnated on MCM-41.

To study the effect of varying the metal loading on the supports, copper was chosen because it gave the highest yield amongst the MCM-41-supported catalysts. Catalysts having 0.5, 1.0, 2.0, and 5.0 wt% of copper on both MCM-41 and activated carbon were compared; the results are given in Figures 8a and 8b. The conversion of benzene and the selectivity to phenol are given in Figure 8a for the copper-on-MCM-41 catalyst and in Figure 8b for the copper-on-activated-carbon catalyst. The yield of phenol is shown in Figure 9.

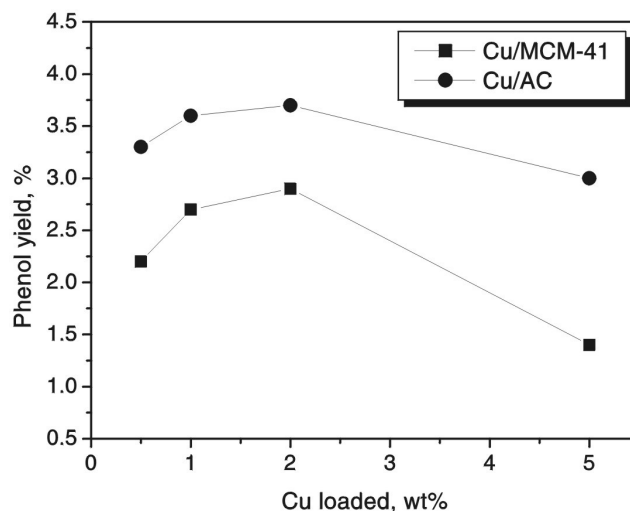
The decrease in the conversion of benzene upon increasing the metal loading beyond 1.0 wt% copper on

**Table 3.** Comparison of Activity with Cu/MCM-41 and Cu/AC Catalysts

| Cu, wt% | Cu-MCM-41 catalysts |      |     | Cu-AC catalysts |      |     |
|---------|---------------------|------|-----|-----------------|------|-----|
|         | X                   | S    | Y   | X               | S    | Y   |
| 0.5Cu   | 5.6                 | 39.8 | 2.2 | 6.2             | 53.5 | 3.3 |
| 1.0Cu   | 7.5                 | 35.8 | 2.7 | 10.1            | 35.4 | 3.6 |
| 2.0 Cu  | 6.9                 | 41.6 | 2.9 | 7.8             | 48.0 | 3.7 |
| 5.0 Cu  | 2.7                 | 51.1 | 1.4 | 5.3             | 56.6 | 3.0 |

**Figure 8(a).** The benzene conversion and selectivity to phenol with Cu/MCM-41 catalysts.**Figure 8(b).** The benzene conversion and selectivity to phenol with Cu/AC catalysts.

both the MCM-41- and activated carbon-supported catalysts can be attributed to the fact that when the metal loading increased, the BET surface area decreased. That is, some of the pore mouths might have become closed, thereby preventing access of the reactants to active sites in those blocked pores. Agglomeration of copper also could be one of the reasons (as seen from the SEM images) for the decrease in the conversion of benzene at higher loadings

**Figure 9.** Variation of yield of phenol with Cu loading on MCM-41 and AC catalysts.

of copper. The relationship between conversion and selectivity is very typical of series parallel-type reactions; the hydroxylation of benzene to phenol is one such reaction. In this type of reaction as conversion increases, the selectivity towards the intermediate product (phenol in this case) decreases.

Comparing the conversion of benzene, we observe that it is higher when using the activated carbon-supported catalysts than when using MCM-41-supported catalysts (Table 3). The results of our benzene adsorption studies indicate that activated carbon is more hydrophobic and, thereby, it adsorbs more benzene, which leads to a slightly higher conversion of benzene on these catalysts when compared to the MCM-41-supported catalysts.

A comparison of the selectivity towards phenol (Table 3) indicates that the activated carbon-supported catalysts are better than the MCM-41-supported catalysts. Methanol adsorption studies have indicated that MCM-41 is more hydrophilic than the activated carbon-supported catalysts. Phenol, being a polar substance, has higher affinity for hydrophilic surfaces and, thereby, becomes converted to higher hydroxylated products, like hydroquinone, benzoquinone, and other products, on the MCM-41-supported catalysts, which leads to a lower selectivity towards phenol observed when using these catalysts.

The results obtained by other researchers for studies of

**Table 4.** Comparison of Performance of Various Catalysts Reported in the Open Literature for the Hydroxylation of Benzene to Phenol

| Catalyst  | Reaction Conditions                        | Conversion, Selectivity, & Yield  | Remarks  | Reference |
|---|--|---|--|-----------|
| Polymer-bound Vanadyl acetylacetonate                             | 70°C<br>30% H <sub>2</sub> O <sub>2</sub>  | Y = 10.0%   | Liquid phase with H <sub>2</sub> O <sub>2</sub> as oxidant | 23        |
| TS-1  | 60°C<br>30% H <sub>2</sub> O <sub>2</sub>  | X = 74.4 %<br>S = 85.6 %<br>Y = 63.7 %  | Liquid phase with H <sub>2</sub> O <sub>2</sub> as oxidant | 24        |
| V on MCM-41 and MCM-48  | 70°C<br>30% H <sub>2</sub> O <sub>2</sub>  | X = 1.39, S = 93%, Y = 1.29 % on MCM-41<br>X = 0.44 %, S = 93%, Y = 0.41% on MCM-48 | Liquid phase with H <sub>2</sub> O <sub>2</sub> as oxidant | 28        |
| AMM catalyst<br>Fe <sub>3</sub> <sup>Me</sup> Si <sub>50</sub> Si | 60°C,<br>30% H <sub>2</sub> O <sub>2</sub> | X = 16.6%<br>S = 63.86 %<br>Y = 10.6 %  | Liquid phase with H <sub>2</sub> O <sub>2</sub> as oxidant | 30        |
| AMM catalyst<br>Cu <sub>3</sub> Si                                | 60°C,<br>30% H <sub>2</sub> O <sub>2</sub> | X = 7.1 %<br>S = 21.13 %<br>Y = 1.5 %   | Liquid phase with H <sub>2</sub> O <sub>2</sub> as oxidant | 30        |
| Ti-MCM-41   | 65°C<br>30% H <sub>2</sub> O <sub>2</sub>  | X = 92%<br>S = 95%<br>Y = 87.4%   | Liquid phase with H <sub>2</sub> O <sub>2</sub> as oxidant | 31        |
| Fe-in TS zeolite  | 400°C<br>N <sub>2</sub> O                  | X <sub>N<sub>2</sub>O</sub> = 96 %<br>Phenol Productivity = 13.4 mmol/gh            | Gas phase with N <sub>2</sub> O as oxidant                 | 6         |
| Fe-modified TS-1  | 400°C<br>N <sub>2</sub> O                  | X <sub>N<sub>2</sub>O</sub> = 96 %<br>S = 95 %<br>Phenol Productivity = 9.4 mmol/gh | Gas phase with N <sub>2</sub> O as oxidant                 | 7         |
| Fe-silicalite   | 450°C<br>N <sub>2</sub> O                  | X = 12.0 %<br>S = 98.0 %<br>Y = 11.76 %   | Gas phase with N <sub>2</sub> O as oxidant                 | 8         |
| Cu- ZSM-5   | 400°C<br>O <sub>2</sub>                    | Y = 1.2 %   | Gas phase with O <sub>2</sub> as oxidant                   | 11        |
| Pt-VO <sub>x</sub> &<br>Pd-VO <sub>x</sub>                        | 140°C<br>O <sub>2</sub> & H <sub>2</sub>   | X = 1.0 %<br>S = 97.0 %<br>Y = 0.97 %   | Gas phase with O <sub>2</sub> as oxidant                   | 12        |
| HPA & Pd in VPI-5 and MCM-41                                      | 130°C<br>O <sub>2</sub> at 60 bar          | X = 5.8 %<br>S = 82.0 %<br>Y = 4.73 %   | Gas phase with O <sub>2</sub> as oxidant                   | 17        |
| Cu-zeolites   | 30°C<br>O <sub>2</sub>                     | Y = 1.69%   | Liquid phase with O <sub>2</sub> as oxidant                | 14        |
| Pd on SiO <sub>2</sub>  | 45°C<br>O <sub>2</sub> & H <sub>2</sub>    | X = 7.0 %<br>S = 88.2 %<br>Y = 6.2 %  | Liquid phase with O <sub>2</sub> as oxidant                | 15        |
| CuO-Al <sub>2</sub> O <sub>3</sub>                                | 30°C<br>O <sub>2</sub>                     | Y = 1.0 %   | Liquid phase with O <sub>2</sub> as oxidant                | 18        |
| V, Pt on SiO <sub>2</sub>   | 60°C<br>O <sub>2</sub> & H <sub>2</sub>    | S <sub>O<sub>2</sub></sub> = 26.2%<br>Rate = 0.288 mmol/h                           | Liquid phase with O <sub>2</sub> as oxidant                | 19        |
| V on SiO <sub>2</sub><br>V on MCM-41                              | 30°C<br>O <sub>2</sub> & H <sub>2</sub>    | Y = 8.2 % V/SiO <sub>2</sub><br>Y = 8.6 % on V/MCM-41                               | Liquid phase with O <sub>2</sub> as oxidant                | 20        |

various catalysts in the hydroxylation of benzene to phenol are presented in Table 4. We observe that the yield of phenol varies from 0.41 to 87.4%. The highest yield obtained in the present study was 3.9% when using the vanadium-impregnated activated carbon catalyst. This study provides a large scope for improvement of the performance of these catalysts by varying the vanadium loading and also by modifying the surface hydrophobicity/hydrophilicity. Further work is being carried out to improve the performance of activated carbon-based catalysts for the hydroxylation of benzene.

### Conclusion

In summary, we have shown that transition metals supported on activated carbon have higher activity for the hydroxylation of benzene to phenol, relative to transition metals supported on MCM-41. The activity of transition metals supported on activated carbon for the production of phenol increased in the order  $V > Fe > Cu$ . A catalyst comprising 2.0 wt% copper on activated carbon gave the highest yield of phenol (3.7%); MCM-41, 2.0 wt% copper gave the highest yield of phenol (2.9%). The higher activity shown by the catalysts containing transition metals supported on activated carbon, relative to MCM-41-supported catalysts, may be attributed to the surface hydrophobicity of activated carbon. In conclusion, activated carbon can be used as an effective support for the transition metal-catalyzed hydroxylation of benzene to phenol.

### Acknowledgments

This work was supported by the International Joint Research Program funded by the Ministry of Science and Technology of Korea.

### References

1. M. Iwamoto, J. I. Irata, K. Matsukami, and S. J. Kagawa, *J. Phys. Chem.*, **87**, 903 (1983).
2. Y. Ono, E. Suzuki, and K. Nakashiro, *Chem. Lett.*, 953 (1988).
3. G. I. Panov, G. A. Sheveleva, A. S. Kharitonov, V. N. Ramannikov, and C. A. Vostrikova, *Appl. Catal. A: General*, **82**, 31 (1992).
4. V. I. Sobolev, K. A. Dubkov, E. A. Paukshtis, L. V. Pirutko, M. A. Rodkin, A. S. Kharitonov, and G. I. Panov, *Appl. Catal. A: General*, **141**, 185 (1996).
5. M. Hfele, A. Reitzmann, D. Roppelt, and G. Emig, *Appl. Catal. A: General*, **150**, 153 (1997).
6. L. V. Pirutko, V. S. Chernyavsky, A. K. Uriarte, and G. I. Panov, *Appl. Catal. A: General*, **227**, 143 (2002).
7. L. V. Pirutko, A. K. Uriarte, V. S. Chernyavsky, A. S. Kharitonov, and G. I. Panov, *Micropor. Mesopor. Mater.*, **48**, 345 (2001).
8. R. Leanza, I. Rossetti, I. Mazzola, and L. Forni, *Appl. Catal. A: General*, **205**, 93 (2001).
9. H. Orita, Y. Hayakawa, M. Shimizu, and K. Takehira, *J. Mol. Catal.*, **42**, 99 (1987).
10. L. C. Passoni, A. T. Cruz, R. Buffon, and U. Schuchardt, *J. Mol. Catal., A: Chemical*, **120**, 117 (1997).
11. H. Yamanaka, R. Hamada, H. Nibute, S. Nishiyama, and S. Tsuruya, *J. Mol. Catal. A: Chemical*, **178**, 89 (2002).
12. H. Ehrich, H. Berndt, M. M. Pohl, K. Jhnisch, and M. Baerns, *Appl. Catal. A: General*, **230**, 271 (2002).
13. E. Kimura, S. Sakonaka, R. Machida, and M. Kodama, *J. Am. Chem. Soc.*, **104**, 4255 (1982).
14. T. Ohtani, S. Nishiyama, S. Tsuruya, and M. Masai, *J. Catal.*, **155**, 158 (1995).
15. T. Miyake, M. Hamada, Y. Sasaki, and M. Oguri, *Appl. Catal. A: General*, **131**, 33 (1995).
16. J. Okamura, S. Nishiyama, S. Tsuruya, and M. Masai, *J. Mol. Catal. A: Chemical*, **135**, 133 (1998).
17. L. C. Passoni, F. J. Luna, M. Wallau, R. Buffon, and U. Schuchardt, *J. Mol. Catal. A: Chemical*, **134**, 229 (1998).
18. T. Miyahara, H. Kanzaki, R. Hamada, S. Kuroiwa, S. Nishiyama, and S. Tsuruya, *J. Mol. Catal. A: Chemical*, **176**, 141 (2001).
19. T. Miyake, M. Hamada, H. Niwa, M. Nishizuka, and M. Oguri, *J. Mol. Catal. A: Chemical*, **178**, 199 (2002).
20. Y. Masumoto, R. Hamada, K. Yokota, S. Nishiyama, and S. Tsuruya, *J. Mol. Catal. A: Chemical*, **184**, 215 (2002).
21. K. Sakai, and K. J. Matsumoto, *J. Mol. Catal.*, **67**, 7 (1991).
22. K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu, and Y. Shimizu, *J. Mol. Catal. A: Chemical*, **114**, 181 (1996).
23. A. Kumar Jr., S. K. Das, and A. Kumar, *J. Catal.*, **166**, 108 (1997).
24. A. Bhaumik, P. Mukherjee, and R. Kumar, *J. Catal.*, **178**, 101 (1998).
25. R. Kumar, P. Mukherjee, and A. Bhaumik, *Catal. Today*, **49**, 185 (1999).
26. E. A. Karakhanov, T. Yu. Filippova, S. A. Martynova, A. L. Maximov, V. V. Predeina, and I. N. Topchieva, *Catal. Today*, **44**, 189 (1998).
27. K. Nomiya, Y. Nemoto, T. Hasegawa, and S. Matsuoka, *J. Mol. Catal. A: Chemical*, **152**, 55 (2000).
28. C. W. Lee, W. J. Lee, Y. K. Park, and S. E. Park, *Catal. Today*, **61**, 137 (2000).



29. J. He, W. P. Xu, D. G. Evans, X. Duan, and C. Y. Li, *Micropor. Mesopor. Mater.*, **44-45**, 581 (2001).
30. M. Stockmann, F. Konietzki, J. V. Nothels, J. Voss, W. Keune, and W. F. Maier, *Appl. Catal. A: General* **208**, 343 (2001).
31. H. Jing, Z. Guo, H. Ma, D. G. Evans, and X. Duan, *J. Catal.* **212**, 22 (2002)
32. A. S. Araujo and M. Jaroniec, *Thermochim. Acta*, **363**, 175 (2000).