

Gas-phase catalytic oxidation of benzene over Cu-supported ZSM-5 catalysts: an attempt of one-step production of phenol

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Abstract

The gas-phase catalytic oxidation of benzene over Cu-supported ZSM-5 catalysts was studied using molecular oxygen as an oxidant. Main products were carbon oxides (CO₂ + CO) and phenol. Phenol was formed only when using ZSM-5 type zeolite as a support. Cu ion-exchanged HZSM-5 (Cu-HZSM-5) zeolite had higher catalytic activity for phenol formation than the NaZSM-5 counterpart (Cu-NaZSM-5). A Cu-HZSM-5 zeolite with larger Si/Al atomic ratio was found to inhibit the formation of carbon dioxides and increase the selectivity of phenol formation. The deactivation of the Cu-HZAM-5 zeolite was recovered by calcination at 773 K in air flow. Cu⁺ species on the zeolite were suggested to play an important role for phenol formation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cu-supported H-ZSM-5 and NaZSM-5 zeolites; Oxidation; Benzene; Phenol; Cu ions

1. Introduction

Phenol has been well known to be one of the most important chemicals among the fields of resin, fiber, and medicine. The recent focus on the direct synthesis of phenol from benzene has occurred, not only from the point of view of an organic synthesis, but also from a chemical industrial point of view. Phenol production in the chemical industry is now mainly carried out through the Cumene process in which three process steps are included, and acetone is produced as a by-product. The economic efficiency of this Cumene process strongly depends on the demand for acetone in the chemical market. It is desirable to directly

produce phenol from benzene via only one-step, which is economically favorable. Lindsay Smith and Norman [1] have previously reported the liquid-phase oxidation of benzene with ferric sulfate–hydrogen peroxide (Fenton's reagent). Also, a phenol synthesis has been reported [2] using a ferric ion–hydrogen peroxide–catechol system (Hamilton' reagent) and this reaction system has been compared with some enzymatic reactions. These previously mentioned reaction systems have used hydrogen peroxide as an oxidant. More recently, the oxidation of benzene to form phenol using cuprous chloride as a catalyst was reported by Sasaki and co-workers [3–5], in which reaction system, oxygen molecules were used as an oxidant in place of hydrogen peroxide. Cu²⁺ ion-exchanged Y-type zeolites have been reported to be useful as catalysts for the gas-phase oxidation of organic materials [6–15], and copper ions in zeolites

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have been indicated to have redox properties according to physico-chemical measurements [16–20]. We reported the liquid-phase oxidation of benzene with molecular oxygen under atmospheric pressure at room temperature using Cu²⁺ ion-exchanged zeolites [21], MCM-41 [22], and co-precipitated CuO-Al₂O₃ [23] catalysts, in the presence of ascorbic acid as a reducing reagent for Cu ions.

In this study, we attempted the gas-phase catalytic oxidation of benzene over the Cu-supported ZSM-5 catalysts using molecular oxygen as an oxidant in order to inquire into the possibility of the one-step formation of phenol.

2. Experimental

2.1. Catalysts

NaZSM-5 zeolites (Si/Al = 43, 90) were synthesized using Al₂(SO₄)₃ and SiO₂ (water glass #3) as Al and Si sources, respectively and tetrapropyl ammonium bromide ((CH₃CH₂CH₂)₄NBr) as a template, according to a patent [24] except for no NaCl addition. NaY (Si/Al = 2.8) and NaX (Si/Al = 1.4) zeolites were purchased from Tosoh Corp. HZSM-5, HY, and HX were prepared by ion-exchanging three times the corresponding Na-type zeolites with a 1N NH₄NO₃ aqueous solution at 353 K for 6 h followed by drying at 393 K overnight and calcining at 773 K for 10 h in air flow. The percentages of the proton ion-exchanges were >99%. Copper ion-exchange zeolites were prepared by ion-exchanging the corresponding Na- and H-type zeolites at 353 K for 2 h with a prescribed concentration of Cu(CH₃COO)₂·H₂O aqueous solution. Copper ion-exchanged KL (Si/Al = 3.4, Tosoh Corp.) and NaM (Si/Al = 40, JRC-Z-M 20) were also prepared by a similar method. Cu-impregnated Na- and H-type ZSM-5 zeolites, SiO₂ (JRC-SIO-4), and Al₂O₃ (JRC-ALO-4) were prepared with a conventional impregnation method using aqueous Cu(CH₃COO)₂·H₂O solution followed by drying at 393 K overnight and calcining at 773 K for 5 h in air flow. The reduction formulas that convert the amount of Cu wt.% to percentage of Cu ion-exchange ((Cu/2Al) × 100; Cu was assumed as Cu²⁺) are as follows: percentage of Cu ion-exchange = 88.0 × Cu wt.% for Cu-HZSM-5 (Si/Al = 43), percentage of

Cu ion-exchange = 165 × Cu wt.% for Cu-HZSM-5 (Si/Al = 90), percentage of Cu ion-exchange = 89.0 × Cu wt.% for Cu-NaZSM-5 (Si/Al = 43).

2.2. Gas-phase catalytic oxidation of phenol

Benzene (Nakarai Tesque, guaranteed reagent) was used without further purification. Mixed gas of N₂, O₂ and CO (N₂:O₂:CO = 19.75:5:0.25) was purchased from Takachiho Chemical. The oxidation was performed under atmospheric pressure using a conventional continuous flow micro-fixed-bed reactor (Pyrex glass, i.d. = 18 mm). The catalyst was usually pre-treated at 773 K for 2 h in air flow. Before the reaction, the reactor including the pre-treated catalyst was purged with N₂ gas for 30 min. The oxidation was started by supplying benzene to the reactor using a micro-feeder. The standard reaction conditions are as follows: $W/F = 4.2 \times 10^2$ g_{cat} min/mol; W (catalyst weight), 0.5 g; F (total flow rate), 1.2×10^{-3} mol/min; reaction temperature, 673 K; benzene:N₂:O₂ = 1.2:20:5 (or benzene:N₂:O₂:CO = 1.2:19.75:5:0.25). The liquid products which were trapped at 223 K with a refrigerant (liquid N₂ + diethyl malonate) were diluted with a mixed solvent of toluene and 2-propanol (v/v, 1:1). The phenol produced was analyzed with a GLC equipped with an FID (Shimazu Model GC-14B or GC-8A) using a 4-m stainless steel column packed with silicon OV-17 at 453–493 K under a N₂ carrier. A 1.5-m stainless steel column packed with Thermon-3000 5% on SHINCARBON A at 473 K was used under a N₂ carrier for hydroquinone. The gaseous products were analyzed by intermediate cell method with a GLC equipped with a TCD (Shimazu Model GC-8A) using stainless steel columns containing silica gel (1 m) and molecular sieve 5 A (1 m) at 393 and 298 K, respectively under H₂ carrier. Yields of benzene, CO₂, and CO were defined as follows:

$$\begin{aligned} \text{yield of phenol (\%)} &= \frac{[\text{mole number of phenol produced}]}{[\text{mole number of benzene fed}]} \times 100 \quad (1) \end{aligned}$$

$$\begin{aligned} \text{yield of CO}_2 \text{ (\%)} &= \frac{(1/6) \times [\text{mole number of CO}_2 \text{ produced}]}{[\text{mole number of benzene fed}]} \times 100 \quad (2) \end{aligned}$$

yield of CO (%)

$$= \frac{(1/6) \times [\text{mole number of CO produced}]}{[\text{mole number of benzene fed}]} \times 100 \quad (3)$$

3. Results and discussion

Various Cu-supported oxides including zeolites were used as catalysts for the gas-phase catalytic oxidation of benzene. All the applied oxides, SiO₂, SiO₂·Al₂O₃, Al₂O₃, NaY, HY, NaX, HX, NaM, and KL, except NaZSM-5 and HZSM-5, were ineffective catalytic supports for the phenol formation. The Cu ion-exchanged (Cu-HZAM-5) and/or impregnated HZSM-5 (Cu/HZSM-5) and the Cu ion-exchanged NaZSM-5 (Cu-NaZSM-5) were found to have catalytic activity for the phenol formation (Table 1). The Cu species supported on the zeolites are the active ones because Na and HZSM-5 supports without Cu species have no catalytic activity for phenol formation. The Cu ions supported on ZSM-5 type zeolites have been reported [19,20] to be more easily reduced than the faujasite-type zeolites [18] with the lower Si/Al ratios. Thus, the Cu²⁺ ions in a ZSM-5 zeolite and in a Y-type zeolite have been reported to begin to reduce to Cu⁺ ions on evacuation at 313 K [19] and at >650 K [18], respectively. The Cu ions in faujasite-type zeolites may be difficult to be reduced in the reaction temperature of 673 K under atmosphere pressure. Cu species supported on Al₂O₃ and SiO₂ have been also reported to be relatively hard to be reduced on the basis of H₂-TPR [18] and CO adsorption [25]

Table 1
Benzene oxidation over Cu-supported ZSM-5 type catalysts^a

Catalyst ^b	Cu-supported (wt.%)	Yield (%)		
		Phenol	CO ₂	CO
Cu/NaZSM-5(43)	0.50	–	53	7.4
Cu/HZSM-5(43)	0.50	0.81	2.1	1.6
Cu-NaZSM-5(43)	1.1	0.50	5.0	2.5
Cu-HZSM-5(43)	0.94	0.88	4.8	2.6
Cu-HZSM-5(90) ^c	0.93	1.2	3.0	1.8
HZSM-5	–	–	0.54	0.37
NaZSM-5	–	–	0.33	Trace

^a Catalyst, 0.5 g; W/F = 4.2 × 10² g_{cat} min/mol; N₂:O₂: benzene = 20:5:1.2; reaction temperature, 673 K.

^b Si/Al atomic ratio of NaZSM-5 and HZSM-5, 43.

^c Si/Al atomic ratio of HZSM-5, 90.

measurements, respectively. The obtained reaction results suggest that the Cu species which are present on the support as reduced state such as Cu⁺ ions, rather than the Cu²⁺ ions, will play an important role in phenol formation. In this report, we studied only the catalytic behavior of the Cu-supported ZSM-5 type catalysts in the subsequent part.

The dependence of phenol yield on the time on stream was investigated using Cu-HZSM-5(43) (Si/Al = 43) catalysts with various Cu contents (Fig. 1). The lower Cu (0.22–0.56 wt.%) ion-exchanged HZSM-5(43) catalysts required the longer time on stream (1.5–4 h) for achieving a steady yield of phenol. The decrease in phenol yield was observed from the time on stream of 0.5–1 h using higher Cu (>0.93 wt.%) ion-exchanged HZAM-5(43) catalysts.

The reactivation of the deactivated Cu (0.93)-HZAM-5(43) (Cu, 0.93 wt.%) catalyst was attempted by calcining the used catalyst at 773 K for 7 h (Fig. 2, solid line). The phenol yield was almost perfectly recovered after the calcination treatment, during which treatment the evolution of CO₂ was observed. The results indicate that the carbonaceous materials

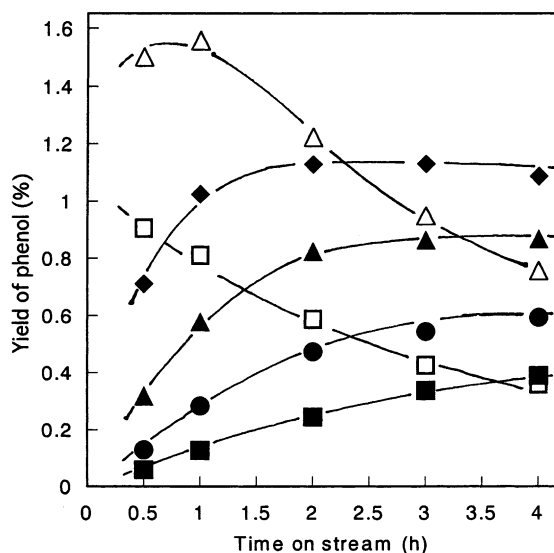


Fig. 1. Relationship between yield of phenol and time on stream using Cu-HZAM-5(43) catalyst. Catalyst, Cu-HZAM-5(43) (Si/Al = 43), 0.5 g; W/F = 4.2 × 10² g_{cat} min/mol; N₂:O₂: benzene = 20:5:1.2; reaction temperature, 673 K; amount of ion-exchanged Cu: (■), 0.22 wt.%; (●), 0.29 wt.%; (▲), 0.45 wt.%; (◆), 0.56 wt.%; (△), 0.93 wt.%; (□), 1.4 wt.%.

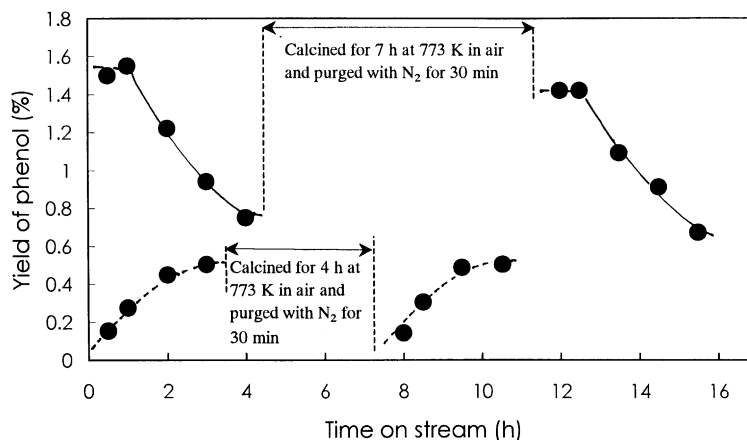


Fig. 2. Behavior of the used Cu-HZSM-5(43) catalyst treated by calcination in benzene oxidation. $W/F = 4.2 \times 10^2 \text{ g}_{\text{cat}} \text{ min/mol}$; $\text{N}_2:\text{O}_2:\text{benzene} = 20:5:1.2$; reaction temperature, 673 K; calcination, at 773 K in air flow; (—), Cu(0.93)-HZSM-5(43) catalyst, 0.5 g; (---), Cu(0.29)-HZSM-5(43) catalyst, 0.5 g.

adsorbed on the catalysts during the benzene oxidation will be responsible for the deactivation of the catalytic activity for phenol formation. The benzene oxidation was repeated using both the fresh and reactivated low Cu (0.29 wt.%) ion-exchanged HZSM-5(43) (Cu (0.29)-HZSM-5(43)) catalysts, which exhibited induction period (Fig. 2, dotted line). The almost steady-state yield of phenol (at the time on stream of 3 h) in the first reaction decreased by calcining the catalyst as shown in the phenol yield

of the second reaction, but the phenol yield again increased with the time on stream.

The benzene oxidation over the Cu (0.29)-HZSM-5(43) catalyst was conducted (Fig. 3, reaction (2)) in the presence of CO ($\text{N}_2:\text{O}_2:\text{CO}:\text{benzene} = 19.75:5:0.25:1.2$) after the calcination of the catalyst used in the benzene oxidation (Fig. 3, reaction (1)) without added CO. The benzene yield in the presence of added CO (reaction (2)) was about one-half of that of the first reaction. The strong interaction of added

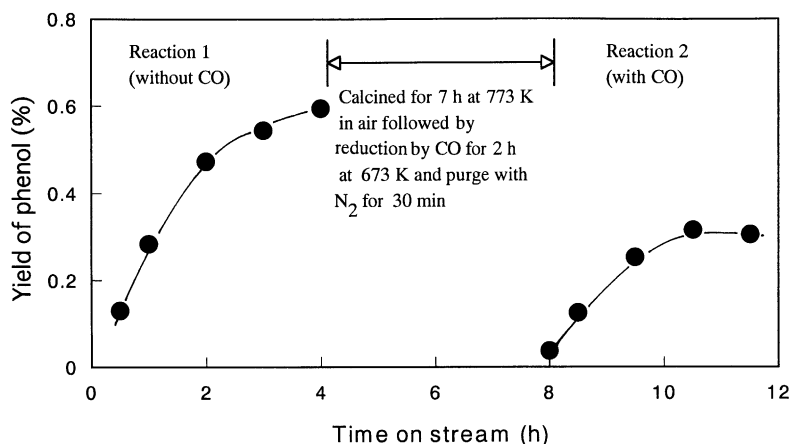


Fig. 3. Influence of CO on the benzene oxidation over Cu(0.29)-HZSM-5(43) catalyst. Catalyst, Cu(0.29)-HZSM-5(43), 0.5 g; $W/F = 4.2 \times 10^2 \text{ g}_{\text{cat}} \text{ min/mol}$; reaction temperature, 673 K; reaction (1), $\text{N}_2:\text{O}_2:\text{benzene} = 20:5:1.2$; reaction (2), $\text{N}_2:\text{O}_2:\text{CO}:\text{benzene} = 19.75:5:0.25:1.2$.

CO with the Cu^+ species [26], which are suggested to be active ones, may inhibit the formation of phenol.

The dependence of the amount of Cu on the yields of both phenol (Fig. 4a) and carbon oxides (Fig. 4b) were investigated using Cu ion-exchanged HZSM-5(43) (Cu-HZSM-5(43)) and NaZSM-5(43) (Cu-NaZSM-5(43)), Cu-impregnated HZSM-5(43) (Cu/HZSM-5(43)) and NaZSM-5(43) (Cu/NaZSM-5(43)) catalysts. The phenol yield catalyzed by the Cu-HZSM-5(43), of which yield was obtained as an average value during 2–4 h of time on stream, increased with the increase in the ion-exchanged Cu and passed through a maximum at the Cu content of around 0.6 wt.% (Fig. 4a, (●)). The yields of carbon oxides ($\text{CO} + \text{CO}_2$) tended to increase beyond the Cu content of around 0.6 wt.% (Fig. 4b, (●), (○)). The oxidation behavior of the Cu-NaZSM-5(43) catalyst (Fig. 4a, (■)) was substantially similar to that of Cu-HZSM-5(43). However, the yield of phenol over the former catalyst tended to become lower than over the latter one at the Cu amounts greater than around 0.5 wt.%, and inversely, the yields of carbon oxides over the Cu-NaZSM-5 catalyst (Fig. 4b, (■), (□)) became higher at greater Cu amounts. The Cu-NaZSM-5 catalyst has been reported to promote more perfect oxidation than the Cu-HZSM-5 catalyst in the ethanol oxidation [27]. The maximum yield of phenol over the Cu/HZSM-5(43) (Fig. 4a, (▲)) was lower than over the Cu-HZAM-5(43) catalyst (Fig. 4a, (●)), and no phenol was produced at a Cu amount >2.5 wt.%. The Cu/HZSM-5(43) catalyst had a greater tendency to increase CO_2 yield (Fig. 4b, (▲)) than the Cu ion-exchanged counterpart (Fig. 4b, (●)). No phenol was yielded over the Cu/NaZSM-5(43) catalyst (Fig. 4a, (◆)). The leveling off of CO_2 yield at a Cu content >0.5 wt.% over the Cu/NaZSM-5 catalyst (Fig. 4b, (◆)) will be due to the almost perfect consumption of supplied oxygen. Among ZSM-5 type zeolites, HZSM-5 zeolite was more effective support for Cu species than NaZSM-5 zeolite (Fig. 4a and b). It was also found that there was an optimum amount of Cu species supported on ZSM-5 zeolite giving a maximum yield of phenol, and Cu-HZSM-5 zeolites with greater Cu amounts had relatively low catalytic activity for phenol formation. The yields of carbon oxides sharply increased over the Cu/HZSM-5 catalysts with higher Cu contents. The Cu species supported by an ion-exchange method had higher catalytic activity for

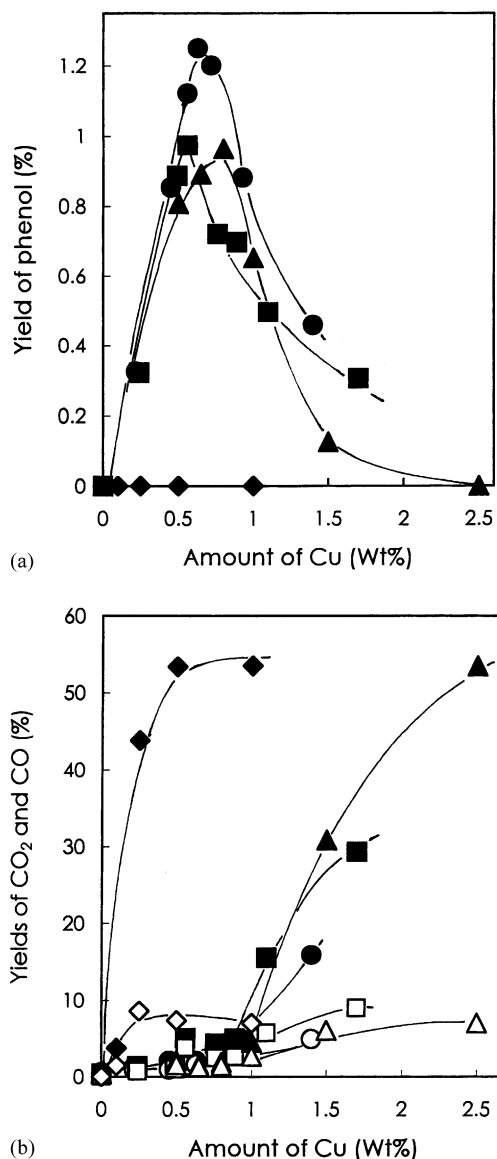


Fig. 4. Dependence of the amount of Cu on the benzene oxidation. $W/F = 4.2 \times 10^2 \text{ g}_{\text{cat}} \text{ min/mol}$; $\text{N}_2:\text{O}_2:\text{benzene} = 20:5:1.2$; reaction temperature, 673 K; (a) phenol formation: catalyst (0.5 g), (●), Cu-HZSM-5(43); (■), Cu-NaZSM-5(43); (▲), Cu/HZSM-5(43); (◆), Cu/NaZSM-5(43); (b) carbon dioxides formation: (●), (■), (▲), (◆), yield of CO_2 ; (○), (□), (△), (◇), yield of CO; (●), (○), Cu-HZSM-5(43); (■), (□), Cu-NaZSM-5(43); (▲), (△), Cu/HZSM-5(43); (◆), (◇), Cu/NaZSM-5(43).

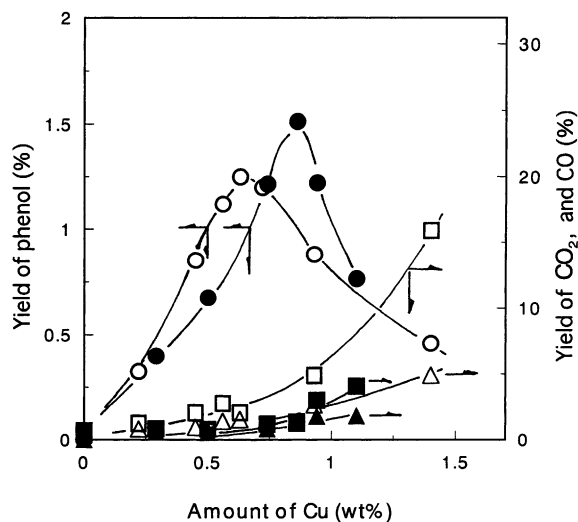


Fig. 5. Influence of Si/Al atomic ratio (43, 90) of HZSM-5 support on the benzene oxidation using Cu-HZSM-5 catalysts: (●), (▲), (■), Cu-HZSM-5(90); (○), (△), (□), Cu-HZSM-5(43); $W/F = 4.2 \times 10^2 \text{ g}_{\text{cat}} \text{ min/mol}$; $\text{N}_2:\text{O}_2:\text{benzene} = 20:5:1.2$; reaction temperature, 673 K; (●), (○), yield of phenol; (▲), (△), yield of CO_2 ; (■), (□), yield of CO.

phenol formation than the Cu species supported by an impregnation method (Fig. 4a).

To investigate the influence of the Si/Al atomic ratio of the HZSM-5 support, whose ratio is a measure of the cloudiness of Cu ions, the oxidation activity of Cu ion-exchanged HZSM-5(90) (Si/Al atomic ratio = 90) (Cu-HZSM-5(90)) was compared (Fig. 5) with that of the Cu-HZSM-5(43). The Cu-HZSM-5(90) had a maximum yield of phenol at a Cu content of around 0.9 wt.%, and the yields of carbon oxides tended to be inhibited at greater Cu amounts. The Cu-HZSM-5(90) had the higher activity for phenol formation and inhibited the formation of carbon oxides, in comparison with the Cu-HZSM-5(43) catalyst. The process time to reach the steady-state yield of phenol, thus, the induction period, was also found to shorten, using the Cu-HZSM-5(90) in place of the Cu-HZSM-5(43) catalyst (Fig. 6). An HZSM-5 support with the higher Si/Al ratio was found to be more desirable for phenol formation and to inversely inhibit the formation of carbon oxides (Fig. 5). All the obtained reaction results suggest that the Cu species which are spatially isolated on the zeolite and are

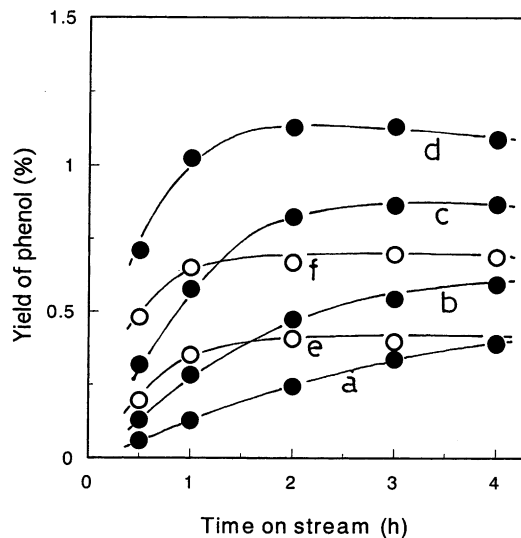


Fig. 6. Relationship between yield of phenol and time on stream using Cu-HZSM-5(43) and Cu-HZSM-5(90) catalysts: (○), Cu-HZSM-5(90); (●), Cu-HZSM-5(43); $W/F = 4.2 \times 10^2 \text{ g}_{\text{cat}} \text{ min/mol}$; $\text{N}_2:\text{O}_2:\text{benzene} = 20:5:1.2$; reaction temperature, 673 K; Cu amount: (a) 0.22 wt.%, (b) 0.29 wt.%, (c) 0.45 wt.%, (d) 0.56 wt.%, (e) 0.29 wt.%, (f) 0.5 wt.%.

easily reducible, rather than aggregated Cu species, are more effective for phenol formation.

4. Conclusions

The gas-phase catalytic oxidation of benzene was performed over various Cu-supported oxide catalysts using gaseous oxygen as an oxidant. Phenol was produced, though the yield was not high, only using the Cu-supported ZSM-5 type zeolites as the catalyst. The Cu species supported on ZSM-5 zeolite were found to have an optimum amount for the formation of phenol. The Cu species supported by the ion-exchange method had a higher catalytic activity for phenol formation than those supported by the impregnation method. HZSM-5 zeolite was a support superior to NaZSM-5 zeolite for phenol formation. Also the Cu-supported catalyst using the HZSM-5 zeolite support with higher Si/Al atomic ratio had the higher catalytic activity and the higher selectivity for phenol formation. The most active catalyst for phenol formation was, thus, Cu ion-exchanged HZSM-5

(Cu-HZSM-5) zeolite with higher Si/Al atomic ratio.

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