

One-Step Oxidation of Benzene to Phenol over Cu/Ti/HZSM-5 Catalysts

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Abstract The gas-phase catalytic oxidation of benzene over copper supported on HZSM-5 added with titanium (Cu/Ti/HZSM-5) was carried out by using molecular oxygen as an oxidant. Phenol was effectively produced by the titanium addition to Cu/HZSM-5. The titanium addition to Cu/HZSM-5 induces the easy reduction of Cu^{2+} species to Cu^+ species in the catalysts, and the produced Cu^+ species seems to produce the phenol effectively.

Keywords Cu/Ti/HZSM-5 · Partial oxidation of benzene · Phenol synthesis

1 Introduction

The partial oxidation of hydrocarbons into various derivatives such as alcohols, aldehydes, ketones, carboxylic acids and epoxides has been extensively investigated, because such products are industrially significant [1–5]. However, the industrial oxidation process usually demands high selectivities, high yields, energy efficiency or economical efficiency. Phenol has been well known to be one of the most important chemicals among the fields of resin, fiber, and medicine. Recently, the direct synthesis of

phenol from benzene has been focused on, not only from the point of view of an organic synthesis, but also from a chemical industrial point of view. Phenol production is currently carried out through the Cumene process or toluene oxidation. Especially, former process which is a most popular process of phenol production consists of three steps and produces acetones as byproduct. The direct oxidation of benzene is more desirable for the phenol production, because of more economical and without byproducts.

The liquid-phase direct hydroxylation of benzene has been reported by Dixon and Norman using ferrous sulfate- H_2O_2 system (Fenton reagent) [6]. The partially exchanged hetero-poly acid has been also reported as a catalyst for the liquid-phase oxidation of benzene in the presence of H_2O_2 oxidation [7, 8]. The gas-phase oxidation of benzene to phenol with N_2O has been actively studied by many authors [9–12]. Especially, Panov et al. have reported that Fe/ZSM-5 effectively catalyze the benzene oxidation to phenol with N_2O [10–12]. However, N_2O is expensive for use as an oxidant on a large scale. Sasaki and co-workers have demonstrated the benzene oxidation to phenol with high selectivity in the presence of both O_2 and H_2 over a supported Cu-Pd binary catalyst. However, the use of a mixture of H_2 and O_2 has the risk of explosion [13, 14]. It has been more recently studied that molecular oxygen directly oxidizes benzene to phenol on various catalysts in the presence of reducing reagent [15–24]. We have previously reported that the supported copper catalysts effectively oxidize the benzene in acetic acid solution to phenol with molecular oxygen in the presence of ascorbic acid as a reducing reagent [22–24]. In these cases, copper ions have been indicated to have redox properties according to physico-chemical measurements [22–28]. However, the direct oxidation of benzene to phenol without reducing reagents is more desirable due to the industrialization.

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We have investigated about the gas-phase direct oxidation of benzene to phenol without reducing reagents. The copper catalysts supported on HZSM-5 or NaZSM-5 have been found to oxidize benzene with only molecular oxygen in the gas-phase [29]. In this catalyst, the obtained yield and selectivity of phenol have been quite low. It has been also reported that the calcination of the Cu/HZSM-5 at the higher temperatures leads to the improvement of phenol formation and the isolated square-pyramidal Cu species is suggested to be the active species for the phenol formation [30]. In this study, we attempt the gas-phase direct oxidation of benzene to phenol with molecular oxygen over Cu/HZSM-5 unmodified and modified by titanium. The effect of titanium addition is investigated in detail.

2 Experimental

HZSM-5 was obtained commercially (ZEOLYST: Si/Al = 29). Ti supported on HZSM-5 (Ti/HZSM-5) was obtained by an impregnation with an aqueous solution of $[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot n\text{H}_2\text{O}$. After the impregnation, the material was dried at 393 K overnight, then calcined at 773 K for 5 h in air flow. The supported Cu catalysts (Cu/HZSM-5 or Cu/Ti/HZSM-5) were also prepared by impregnating either

performed under atmospheric pressure using a conventional continuous flow 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 N_2 gas for 30 min at 773 K. The oxidation was started by supplying benzene to the reactor using a micro-feeder. The standard reaction conditions are as follows: $W/F = 2.36 \times 10^2 \text{ g}_{\text{cat}} \text{ min/mol}$; W (catalyst weight), 0.5 g; F (total flow rate), $2.12 \times 10^{-3} \text{ mol/min}$; reaction temperature, 673 K; benzene: $\text{N}_2:\text{O}_2 = 0.18:4:1$. The liquid products which were trapped at 223 K with a refrigerant (liquid N_2 + diethyl malonate) were diluted with a mixed solvent of toluene and 2-propanol (v/v, 1:1). The liquid products such as phenol, p-benzoquinone, and hydroquinone were analyzed with a liquid chromatograph (Jasco, LC-2000 Plus) using a C18 column (0.15 m) under the mixed solution carrier of 0.1 vol% trifluoroacetic acid aq. and acetonitrile (v/v, 4:6). The gaseous products such as CO and CO_2 were analyzed with a gas chromatograph equipped with TCD using a stainless steel columns containing active carbon (1 m), active carbon (4 m) and molecular sieve 5A (1 m) at 413 K, room temperature, and room temperature, respectively under H_2 carrier. Yield of benzene, p-benzoquinone, hydroquinone, CO or CO_2 was defined as follows:

yield of phenol, p-benzoquinone, or hydroquinone (%)

$$= \frac{[\text{mole number of phenol, p-benzoquinone, or hydroquinone produced}]}{[\text{mole number of benzene fed}]} \times 100 \quad (1)$$

HZSM-5 or Ti/HZSM-5 with an aqueous solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. After the impregnation, the catalyst was dried at 393 K overnight, then calcined at 1,273 K in air flow for 5 h. The samples will be designated as $n \text{ wt}\%$ Cu/HZSM-5 or Cu/Ti/HZSM-5 [$\text{Ti}/\text{Cu} = m$] where n represents the content of copper ($n = 0.7$) and m represents Ti/Cu atomic ratio ($m = 0, 0.4, 0.5, 0.7, \text{ and } 1.0$).

yield of CO or CO_2 (%)

$$= \frac{(1/6) \times [\text{mole number of CO, or } \text{CO}_2 \text{ produced}]}{[\text{mole number of benzene fed}]} \times 100 \quad (2)$$

Yield of partial oxidation products was also defined as follows:

yield of partial oxidation products(%)

$$= \frac{[\text{sum total of mole number of phenol, p-benzoquinone, or hydroquinone produced}]}{[\text{mole number of benzene fed}]} \times 100 \quad (3)$$

Benzene (Nakarai Tesque, guaranteed reagent) was used without further purification. The oxidation of benzene was

The amounts of CO adsorption on the catalysts were measured as follows: Sample (0.05 g) was calcined at

773 K in O₂ (2.6 kPa) for 1 h in the quartz cell connected to the vacuum systems. It was cooled to the reaction temperature (673 K) with O₂, and evacuated under vacuum condition (10⁻² Pa) for 2 h, and then the dead volume of this sample was measured by using He gas. The sample was re-evacuated under vacuum condition for 0.5 h at 673 K, then CO gas (2.6 kPa) was induced to the sample at 673 K. The amount of adsorbed CO was estimated by the measurements of pressure change.

X-ray absorption fine structure (XAFS) spectra for the samples were taken at room temperature in fluorescence mode for K-edge of Cu at the beam-line BL01B1 of SPring-8. After the calcination of samples at 773 K for 1 h, the samples also were sealed with polyethylene films in nitrogen atmosphere. Fourier transformations for Cu samples were performed on k³-weighted EXAFS oscillations in the range of 3–12 Å⁻¹. Electron spin resonance spectra of Cu/HZSM-5 and Cu/Ti/HZSM-5 catalysts were measured at room temperature with a JEOL JES-TE300 X band-spectrometer. Prior to ESR measurements, samples were calcined at 773 K for 1 h in O₂, followed by evacuation at room temperature or 773 K for 2 h at 10⁻² Pa. The magnetic field was corrected by using a manganese maker.

3 Results and Discussion

Cu/HZSM-5 and Cu/Ti/HZSM-5 catalysts oxidized benzene to phenol, hydroquinone, p-benzoquinone, CO, and CO₂. No formation of oxidation products was observed over the catalysts unsupported with Cu, such as HZSM-5 and Ti/HZSM-5. The phenol yield during the oxidation of benzene over Cu/HZSM-5 and Cu/Ti/HZSM-5 catalysts is shown in Fig. 1. Titanium addition to Cu/HZSM-5 catalyst is found to cause the increase of phenol yield. In this case, the selectivity of phenol formation also improved by the Ti addition to Cu/HZSM-5. The maximum phenol yield of Cu/HZSM-5 is obtained at the time on stream of 100 min, whereas Cu/Ti/HZSM-5 catalyst provides maximum that at the reaction time of 80 min. It was previously reported that the redox cycle of between Cu⁺ and Cu²⁺ was related with the formation of oxidation products [29, 30]. The induction period may be due to the generation of Cu⁺ from Cu²⁺ species. Hence, it is decided to estimate the yield of the every product in the point of time which is got a maximum phenol yield. Figure 2a also shows the yield of every product until 4 h of the time on stream. The yield of partial oxidation products, such as phenol, hydroquinone, and p-benzoquinone, gradually decrease with the time on stream. On the other hand, yield of CO and CO₂ continuously increase. The re-calcination treatment of the used Cu/Ti/HZSM-5 catalyst leads to the significant recovery of partial oxidation yield (see Fig. 2b). The carbon deposit is

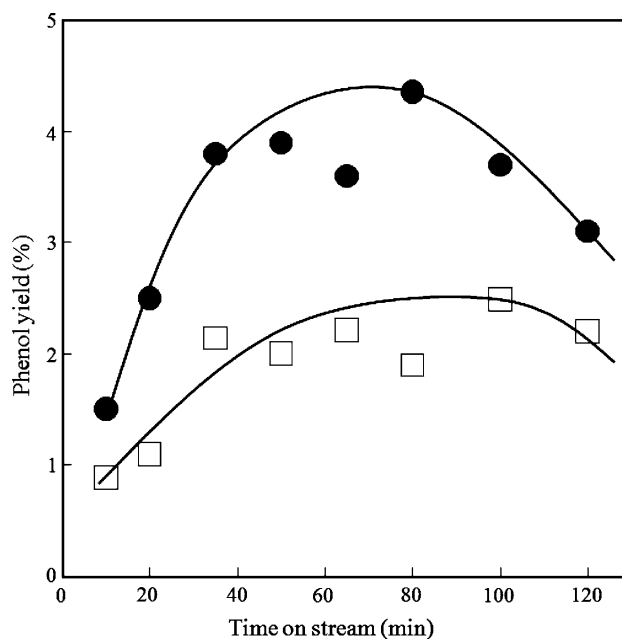


Fig. 1 Time profile of phenol yield for the oxidation of benzene over Cu/HZSM-5 (open square) and Cu/Ti/HZSM-5 (filled circle). Catalyst, Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Ti/Cu = 0.7, Si/Al = 29), Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Si/Al = 29)

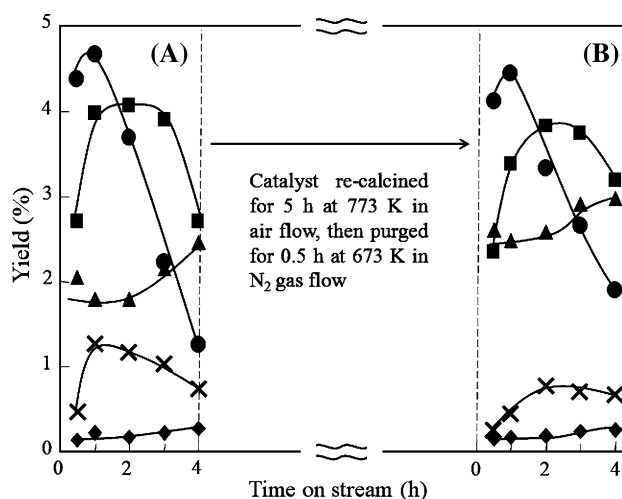
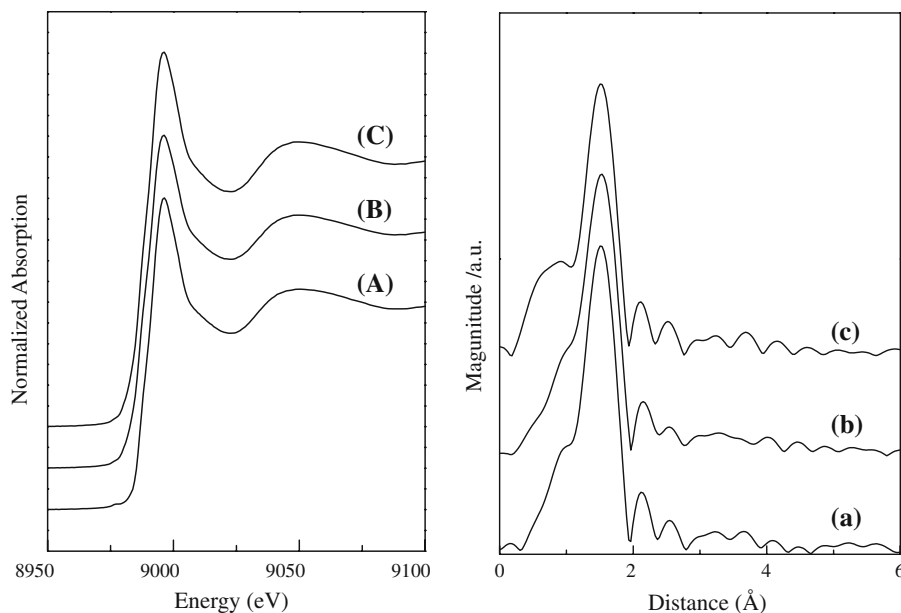


Fig. 2 Time profile of product yields for the oxidation of benzene over (A) fresh and (B) re-calcined Cu/Ti/HZSM-5 catalysts. Re-calcined catalyst was obtained by the calcinations of used catalyst for 5 h at 773 K. Catalyst, Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Ti/Cu = 0.7, Si/Al = 29); Yield of phenol (filled circle), hydroquinone (times), p-benzoquinone (filled square), CO (filled diamond) and CO₂ (filled triangle)

found to suppress the formation of partial oxidation products, and the re-calcination treatment of used catalysts causes desorption of carbon deposit on the catalysts. This indicates that Cu/Ti/HZSM-5 catalysts are reusable by the re-calcination treatment in air flow. Figure 3 also shows the XAFS spectra of Cu/Ti/HZSM-5 catalysts before and after

Fig. 3 XANES [A, B, C] and k^3 -weighted Fourier transforms of EXAFS [a, b, c] of Cu/HZSM-5 (Cu = 0.7 wt%, Si/Al = 29) [A, a], and Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Ti/Cu = 0.7, Si/Al = 29) before [B, b] and after reaction [C, c]



reaction. XANES and Fourier transforms of EXAFS spectra indicate that no significant change of the valency and coordination geometry of Cu species is observed after the reaction. Therefore, these results were demonstrated that the carbon deposit led to the deactivation of phenol formation.

Figure 4 indicates the dependence of the amounts of titanium addition to Cu/HZSM-5 catalysts. As mentioned above, the yield of every product was estimated in the point of time which got a maximum phenol yield. These results indicate that the increase of Ti/Cu atomic ratio until 0.7 leads to the improvement of phenol yield and selectivity. The yields of hydroquinone and p-benzoquinone were also improved by the increase of Ti/Cu atomic ratio. The maximum phenol yield is obtained at 0.7 of Ti/Cu atomic ratio, and then the phenol yield gradually decreases with the increase of Ti/Cu atomic ratio. Hence, phenol yield is optimized at 0.7 of Ti/Cu atomic ratio. Although the yields of hydroquinone and p-benzoquinone show the almost same behavior as phenol yield, CO₂ yield continuously increases with the increase of Ti/Cu atomic ratio. It is speculated that the active site of CO₂ formation is different from that of phenol, hydroquinone and p-benzoquinone.

It is investigated about the relationship between Cu species and the titanium addition to Cu/HZSM-5 in detail. XANES spectra of both Cu/HZSM-5 and Cu/Ti/HZSM-5 catalysts show that there are most as Cu²⁺ species in these catalysts [31] (see Fig. 3). No significant change of the valency and coordination geometry of Cu species is observed by Ti addition. UV–Vis measurements of both catalysts also gave same results as XAFS measurements (figure not depicted). Hence, the almost copper species exists as CuO species in the Cu/HZSM-5 and Cu/Ti/HZSM-5 catalysts. It is known that the evacuation of these

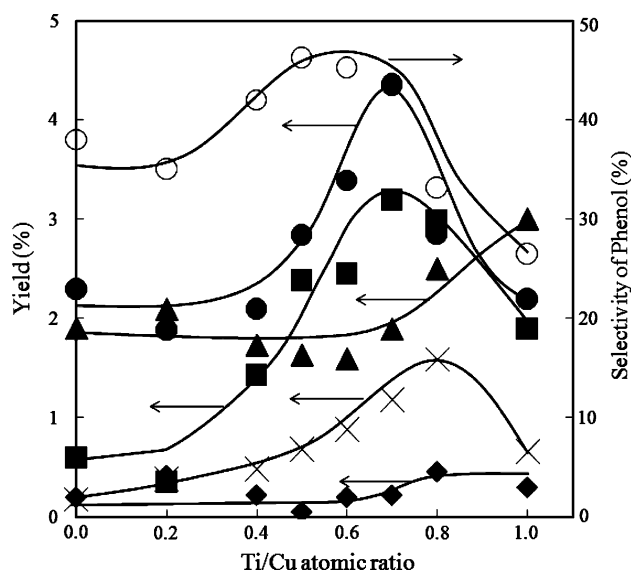


Fig. 4 Dependence of the Ti/Cu atomic ratio of Cu/Ti/HZSM-5 catalysts on the benzene oxidation. Catalyst, Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Ti/Cu = 0–1.0, Si/Al = 29); Yield of phenol (filled circle), hydroquinone (times), p-benzoquinone (filled square), CO (filled diamond) and CO₂ (filled triangle); Selectivity of phenol (open circle)

catalysts at higher temperatures under vacuum condition leads to the formation of Cu⁺ species by reduction of Cu²⁺ species. And, CO gas selectively adsorbs to the Cu⁺ species. In short, the amounts of adsorbed CO to the copper catalysts can imply the amounts of Cu⁺ species which is generated by the reduction treatment under vacuum condition. The relationship between the yield of partial oxidation products and the amount of adsorbed CO to the Cu/Ti/HZSM-5 catalysts for the different Ti/Cu atomic

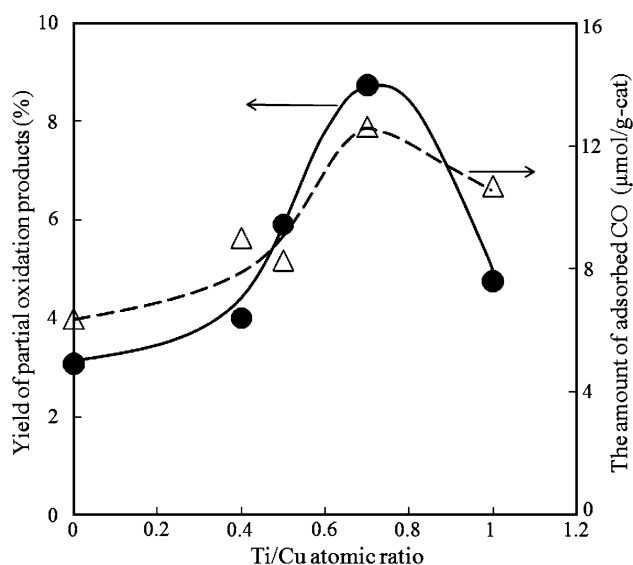


Fig. 5 Relationship between yield of partial oxidation products (filled circle) and the amounts of adsorbed CO (open triangle) on Cu/Ti/HZSM-5 catalysts. Catalyst, Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Ti/Cu = 0–1.0, Si/Al = 29)

ratio was shown in Fig. 5. The amounts of adsorbed CO increase with increasing Ti/Cu atomic ratio, and the maximum amounts of adsorbed CO are obtained at 0.7 of Ti/Cu atomic ratio. This result indicates that Cu species of the Cu/Ti/HZSM-5 catalysts at 0.7 of Ti/Cu atomic ratio is reduced most easily to Cu^+ species. Furthermore, the maximum yield of partial oxidation products over Cu/Ti/HZSM-5 is also obtained by 0.7 of Ti/Cu atomic ratio. It is recognized that the yield of partial oxidation products shows the almost same behavior as the amounts of adsorbed CO. Hence, the yield of partial oxidation products seems to have relation to the amounts of Cu^+ species.

The degree of the reduction of Cu^{2+} species in the Cu/Ti/HZSM-5 is investigated by ESR measurements (Fig. 6). Two signals ($g_{\parallel}^1 = 2.33$, $A_{\parallel}^1 = 157$; $g_{\parallel}^2 = 2.31$, $A_{\parallel}^2 = 159$) are detected in the ESR spectra of Cu^{2+} species for Cu/HZSM-5 and Cu/Ti/HZSM-5, indicating two individual configurations of Cu^{2+} species presence in the Cu/HZSM-5 and Cu/Ti/HZSM-5. Kucherov et al. were reported that these signals were assigned to two square-pyramidal ($g_{\parallel}^1 = 2.33$, $A_{\parallel}^1 = 158$; $g_{\parallel}^2 = 2.31$, $A_{\parallel}^2 = 160$) and a square-planar ($g_{\parallel}^3 = 2.28$, $A_{\parallel}^3 = 171$) Cu^{2+} species [32, 33]. Hence, these signals of Cu/Ti/HZSM-5 are assigned to the square-pyramidal. The intensities of these spectra are decreased by the reduction treatment. In especial, it is obvious that the intensity of Cu/Ti/HZSM-5 significantly decreases by the reduction treatment. The intensity of the reduced Cu/Ti/HZSM-5 was about 40% of the untreated catalyst. As for the reduced Cu/HZSM-5, the peak intensity was about 75% of untreated catalyst. It means that the Cu/Ti/HZSM-5 can be easily reduced in

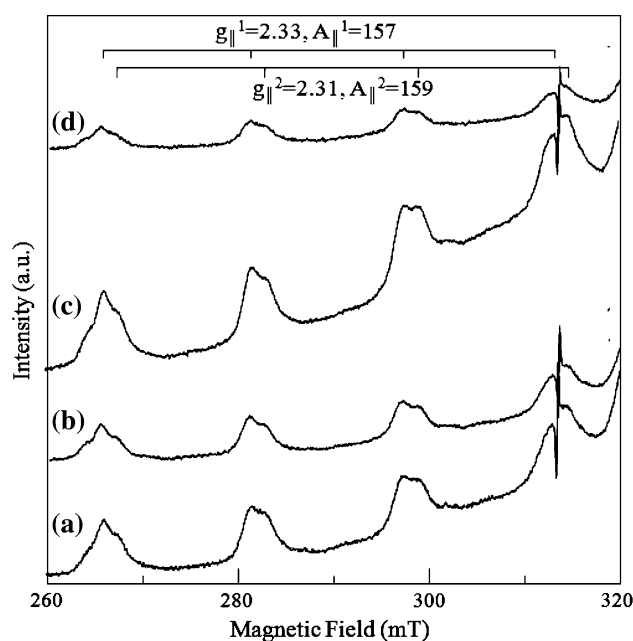


Fig. 6 Parallel component of ESR spectra of Cu^{2+} species for Cu/HZSM-5 (a, b) and Cu/Ti/HZSM-5 (c, d). Both catalysts were calcined at 773 K for 1 h in O_2 , followed by evacuation at room temperature (a, c) or 773 K (b, d) for 2 h at 10^{-2} Pa. Catalyst, Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Ti/Cu = 0.7, Si/Al = 29), Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Si/Al = 29)

comparison with Cu/HZSM-5. We previously reported that Cu^+ species on the zeolite played an important role for phenol formation in the gas-phase direct oxidation of benzene [29, 30]. In this report, it was considered that the redox cycle of Cu^+ and Cu^{2+} caused the partial oxidation of benzene. Hence, the titanium addition to Cu/HZSM-5 seems to induce the easy reduction of Cu^{2+} species to Cu^+ and the produced Cu^+ species may produce the phenol effectively. The excessive addition of titanium to Cu/HZSM-5, however, may inhibit the access of reactant to active Cu sites or may cause the further oxidation of partial oxidation products to CO or CO_2 .

4 Conclusions

The gas-phase catalytic oxidation of benzene was performed over Cu/HZSM-5 catalysts added with titanium using gaseous oxygen as an oxidant. Phenol was effectively produced by the titanium addition to Cu/HZSM-5. Although the phenol yield decreased with passing the time on stream, the re-calcination of the used Cu/Ti/HZSM-5 catalysts was found to cause the recovery of phenol formation. Cu/HZSM-5 catalysts added with titanium were also optimized for the formation of phenol by the Ti/Cu atomic ratio. The measurements of adsorbed CO amounts indicated that the amounts of Cu^+ species in the reduced

Cu/Ti/HZSM-5 catalysts increased with increasing Ti/Cu atomic ratio and the yield of partial oxidation products had relation to the amounts of Cu^+ species. From ESR measurements, it was also found that the titanium addition to Cu/HZSM-5 induce the easy reduction of Cu^{2+} species to Cu^+ . In short, it was speculated that the amounts of redox site which related to the partial oxidation of benzene increased with the titanium addition. The copper catalysts having larger amounts of redox sites seemed to cause the partial oxidation of benzene to phenol effectively.

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