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[Regular Paper]

Relationships between Phenol Production Activities and Lewis Acid Sites of Cu/HZSM-5 Catalyst for Gas-phase Aerobic Benzene Oxidation

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The currently used cumene method of producing phenol is a multistep reaction that requires costly production facilities and a large amount of energy, and thus, a simpler, greener method of phenol production must be developed. This study investigates the acidic properties of HZSM-5 and redox cycle of Cu to examine the mechanism of phenol formation via the gas-phase catalytic oxidation of benzene over the Cu/HZSM-5 catalyst. Pyridine adsorption Fourier transform infrared spectroscopy suggests that calcination at a high temperature (1273 K) leads to the dealumination of Cu/HZSM-5, and extra-framework Al increases the number of Lewis acid sites, which function as benzene activation sites. Photoluminescence spectroscopy indicates that the redox cycle of Cu comprises the reduction of Cu^{2+} to Cu^+ by benzene and the oxidation of Cu^+ to Cu^{2+} by O_2 . Based on these results, the mechanism of phenol formation from benzene is inferred, and this study paves the way for the establishment of the economical, green industrial synthesis of phenol.

Keywords

Benzene oxidation, Phenol synthesis, Supported copper catalyst, MFI zeolite, Reaction mechanism

1. Introduction

Phenol is an essential raw material in the organic chemical industry, as it is used in a wide range of applications, including the development of pharmaceuticals, dyes, housing materials, textiles, and plastics, such as phenol resins. Although a small amount of phenol is obtained via coal tar separation, most is industrially synthesised¹⁾. The current mainstream industrial manufacturing process for phenol is the cumene method, which is a three-step synthetic reaction with cumene as the raw material²⁾. This method provides an overall phenol yield of approximately 5 % and excellent selectivity (>90 %) for phenol formation at each reaction step. In addition, the acetone obtained during the reaction has a high market value. However, as the cumene method is a multistep reaction, it is costly in terms of production facilities, with a considerable environmental impact owing to its high energy consumption. Therefore, a simpler, greener process for use in producing phenol is required. The ideal reaction in

phenol synthesis is a single-step reaction, wherein phenol is formed by directly adding a single O atom to benzene. Generating phenol efficiently via such a direct oxidation reaction should be of industrial significance, but introducing an O atom directly onto the aromatic ring is challenging, as benzene is extremely structurally stable. Furthermore, the phenol generated is more prone to oxidation than benzene and excessive oxidation is likely to proceed. Although numerous studies have investigated the single-step synthesis of phenol, none have afforded superior industrial results than those obtained using the cumene method.

N_2O or O_2 is used as an oxidant in the single-step gas-phase synthesis of phenol from benzene^{3)~19)}. Phenol can be obtained with a high yield and selectivity when N_2O is used, but N_2O is extremely costly. Therefore, our laboratory focused on the gas-phase catalytic oxidation of benzene using low-cost O_2 as the oxidant and investigated catalysts for use in efficiently producing phenol in a single-step reaction. We previously evaluated the activities of Cu-loaded catalysts on various supports in phenol formation, with NaZSM-5 and HZSM-5 as the only effective supports²⁰⁾. Neither NaZSM-5 nor HZSM-5 without loaded Cu exhibited catalytic activity in phenol formation, and thus, Cu was

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the active species²⁰⁾. Subsequently, multiple investigations indicated that Cu^+ produced by reducing the loaded Cu^{2+} formed phenol and the redox cycle between Cu^+ and Cu^{2+} resulted in partial benzene oxidation^{20)~24)}. However, the detailed mechanism of phenol formation from benzene has still not been elucidated, and thus, this study examines the activation of O_2 and benzene in detail to determine the mechanism of phenol formation from benzene.

2. Experimental

2.1. Materials

$\text{NH}_4\text{ZSM-5}$ ($\text{Si}/\text{Al}=29$) was obtained from Zeolyst International (Conshohocken, PA, USA), and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (special grade), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (special grade), benzene (special grade), toluene (special grade), 2-propanol (special grade), NaOH , and tetrapropylammonium bromide (TPABr) were supplied by Nacalai Tesque, Inc. (Kyoto, Japan) and used as received, without further purification. Tetraethyl orthosilicate was purchased from Tokyo Chemical Ind. Co., Ltd. (Tokyo, Japan), and N_2 and O_2 gases were acquired from K.K. Kobe Oxygen (Kobe, Japan).

2.2. Catalyst Preparation

Silicalite was prepared as follows. In a polypropylene cup, a 1.60 mol/L aqueous tetraethyl orthosilicate solution (31.25 mL) was mixed with TPABr (2.018 g) as a structure-directing agent and stirred. Ion-exchanged H_2O (30.86 g) containing NaOH (0.28 g) was then added dropwise, and the mixture was stirred for 1 h until uniform. An autoclave coated with polytetrafluoroethylene was filled with the resulting gel, which was then subjected to hydrothermal synthesis at 423 K for 24 h. The resulting white precipitate was filtered and washed with approximately 3 L of hot H_2O (at approximately 343 K), dried overnight at 393 K, and calcined for 5 h at 773 K in still air to remove the structure-directing agent.

In preparing Cu-loaded HZSM-5 (Cu/HZSM-5), HZSM-5 was first generated by calcining $\text{NH}_4\text{ZSM-5}$ in flowing air (N_2 : 100 mL/min, O_2 : 25 mL/min) for 5 h at 773 K. Subsequently, HZSM-5 (2.00 g) was soaked in a 4.41×10^{-3} mol/L aqueous $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ solution (50 mL), which was then evaporated to dryness at 348 K. It was dried overnight at 393 K and calcined for 5 h at 773–1323 K in flowing air. HZSM-5 was thus loaded with 0.7 wt% Cu to yield Cu/HZSM-5.

Al-loaded HZSM-5 (Al/HZSM-5) was prepared by soaking HZSM-5 (2.00 g) in a 4.44×10^{-3} – 2.22×10^{-2} mol/L aqueous $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution (50 mL), which was then evaporated to dryness at 348 K. The material was dried at 393 K overnight and calcined for 5 h at 773 K in flowing air. The same procedure was employed to prepare Cu/Al/HZSM-5(*x*). Al/HZSM-5 (2.00 g) was soaked in the 4.41×10^{-3} mol/L aqueous

$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ solution (50 mL), which was then evaporated to dryness at 348 K. The material was dried overnight at 393 K and calcined for 5 h at 1273 K in flowing air (*x* represents the amount of loaded Al (wt%)).

Cu- (Cu/silicalite) and Cu-and-Al-loaded silicalite (Cu/Al/silicalite) were prepared using the same procedures as those used in preparing Cu/HZSM-5 and Cu/Al/HZSM-5, respectively.

2.3. Characterisation

X-ray diffraction was conducted using a RINT 2000 (Rigaku Corp., Tokyo, Japan) to evaluate the crystal structures of the prepared catalysts. The light source provided Cu $K\alpha$ radiation and the scans were performed in 0.02° steps in the range $2\theta = 5.0^\circ$ – 55.0° (scan counts = 4.0). N_2 ad-/desorption was performed using a BELSORP MINI (Microtrac, Haan, Germany) to determine the specific surface areas of the catalysts. The samples were pre-treated via calcination for 2 h at 473 K in N_2 flowing at 50 mL/min, and the analysis was conducted at 77 K. The specific surface areas of the catalysts were calculated using the Brunauer-Emmett-Teller (BET) method.

NH_3 temperature-programmed desorption (NH_3 -TPD) was performed using a reduced-pressure static adsorption volume analyser. First, 0.06 g of the catalyst was placed in the apparatus and evacuated for 1 h at 773 K. NH_3 was adsorbed for 0.5 h at 373 K, followed by degassing for another 0.5 h, and then the catalyst was heated to 773 K at 10 K/min to desorb the NH_3 .

Pyridine adsorption Fourier transform infrared (FT-IR) spectroscopy was performed using an FT-IR spectrometer (Nicolet 380, Thermo Fisher Scientific, Waltham, MA, USA) at room temperature (298 K) in the range 1400 – 1560 cm^{-1} (resolution of 4 cm^{-1} , 1000 scans). The milled catalyst (40 mg) was used to form pellets with diameters of 13 mm, which were pre-treated via heating and degassing under vacuum for 2 h at 523 K. FT-IR spectroscopy was then performed before pyridine adsorption. Pyridine was subsequently introduced at 2.5 kPa and 373 K and adsorbed for 0.5 h, and the FT-IR spectrum after pyridine adsorption was obtained after degassing at 523 K for 0.5 h.

The valence states of the Cu loaded on the catalysts were investigated via photoluminescence (PL) spectroscopy using an F-7000 fluorescence spectrophotometer (Hitachi High-Tech Corp., Tokyo, Japan) at 77 K using a 150 W Xe lamp as the light source.

2.4. Gas-phase Catalytic Oxidation of Benzene

A fixed-bed distribution tube reactor comprised of Pyrex with an inner diameter of 18 mm was used in benzene oxidation. In pre-treatment, 0.50 g of the catalyst was calcined for 2 h at 773 K in air flowing at 2.12×10^{-3} mol/min. The catalyst was cooled to 673 K while the reaction tube was purged with N_2 for 30 min.

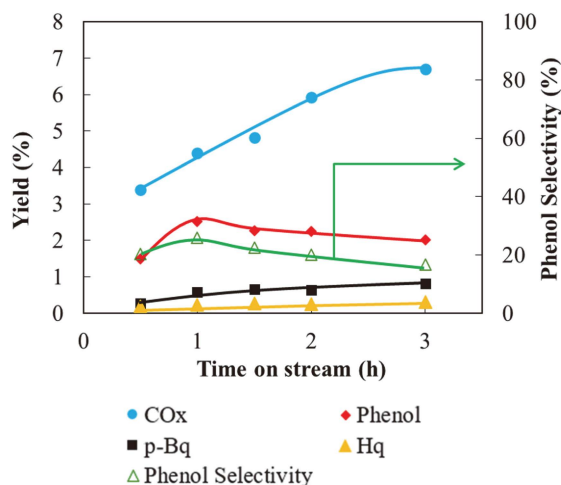


Fig. 1 Time on Stream of Each Product Generated via Benzene Oxidation over Cu/HZSM-5 (calcination temperature: 1273 K, p-Bq: *p*-benzoquinone, Hq: hydroquinone)

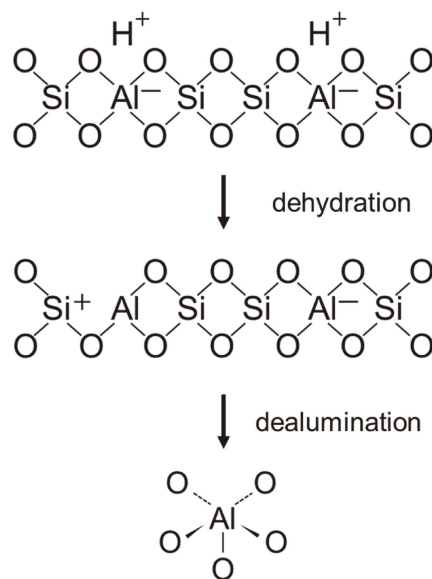
The reaction was then allowed to proceed for 3 h at 673 K by supplying a reaction gas comprising N₂, O₂, and benzene (molar ratio = 4 : 1 : 0.18) at 2.12×10^{-3} mol/min. The products were separated into liquids and gases by cooling the trap tube connected to the reaction tube with a refrigerant comprising diethyl malonate and liquid N₂. The liquid products were quantified using the internal standard method via high-performance liquid chromatography (LC-2000 Plus, JASCO Corp., Tokyo, Japan), and the internal standard used was toluene. The gaseous products were quantified using the external standard method via gas chromatography (GC-8A, Shimadzu Corp., Kyoto, Japan).

The reaction was performed using the reduced catalyst. The catalyst was reduced by baking it in a reduced-pressure static apparatus for 2 h in flowing air at 773 K, introducing CO at 2.7 kPa and 673 K, and leaving the catalyst in the apparatus for 1 h. The reduced catalyst was removed under a vacuum and sealed in the reaction tube in a N₂-purged glove bag.

3. Results and Discussion

3.1. Effects of the Calcination Temperature on the Acidic Properties of the Catalysts

The gas-phase catalytic oxidation of benzene with O₂ was conducted over the Cu/HZSM-5 catalyst. **Figure 1** shows the time on stream of each product of this reaction, and the main products are phenol, *p*-benzoquinone, hydroquinone, and CO₂ and CO (collectively denoted COx). In the following analysis, we focus on phenol. We previously reported that Cu/HZSM-5 calcined at a higher temperature acts as a catalyst, affording improved phenol yields²¹⁾. Supported Cu exhibits two coordination states: square-pyramidal and -planar.



Scheme 1 Dehydration and -alumination of HZSM-5

The proportion of Cu²⁺ in the square-pyramidal coordination state increases with increasing calcination temperature, and thus, Cu/HZSM-5 calcined at higher temperatures provides higher phenol yields. However, the effect of the calcination temperature on the HZSM-5 support has not yet been studied. When HZSM-5, which is a solid acid catalyst, is calcined at high temperatures, its acidic properties change because of dehydration and -alumination, as shown in **Scheme 1**^{25)~27)}. The catalytic activity of HZSM-5 is significantly influenced by its acidic properties^{28)~34)}, and thus, changes in the acid nature of HZSM-5 likely affect its activity in the gas-phase catalytic oxidation of benzene over the Cu/HZSM-5 catalyst. Hence, the effects of the calcination temperature on the acidic properties of the catalysts were investigated via NH₃-TPD and pyridine adsorption FT-IR spectroscopy. **Figure 2** shows the NH₃-TPD profiles of HZSM-5 calcined at different temperatures, and the peak at approximately 400 K is attributed to the desorption of NH₃ physisorbed on HZSM-5. In the profiles of HZSM-5 calcined at temperatures of ≥ 1073 K, peaks are observed at approximately 480 K, which are attributed to the desorption of NH₃ adsorbed on the Al species exposed on the surfaces of the catalysts via dealumination. The peak observed at > 573 K is attributed to the desorption of NH₃ chemisorbed on the acid sites of the catalyst. Furthermore, the intensity of the peak ascribed to NH₃ chemisorbed on the acid sites decreases and the peak position shifts toward higher temperatures when HZSM-5 is calcined at a higher temperature. This suggests that the acidic properties of HZSM-5 change significantly with the calcination temperature. This phenomenon is also observed for Cu/HZSM-5 (**Fig. 3**).

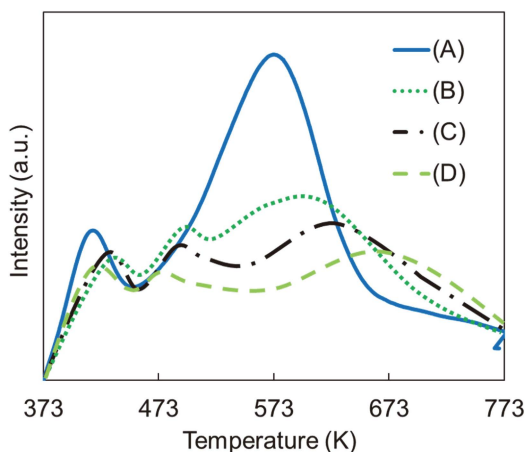


Fig. 2 NH_3 -TPD Profiles of HZSM-5 Calcined at (A) 773, (B) 1073, (C) 1173, and (D) 1273 K

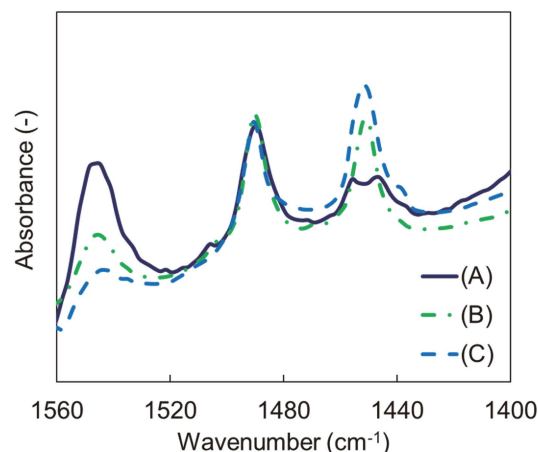


Fig. 4 FT-IR Spectra of Pyridine Adsorbed on Cu/HZSM-5 Calcined at (A) 773, (B) 1073, and (C) 1273 K

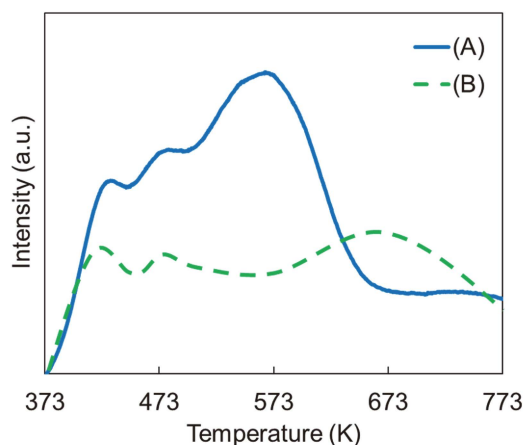


Fig. 3 NH_3 -TPD Profiles of Cu/HZSM-5 Calcined at (A) 773 K and (B) 1273 K

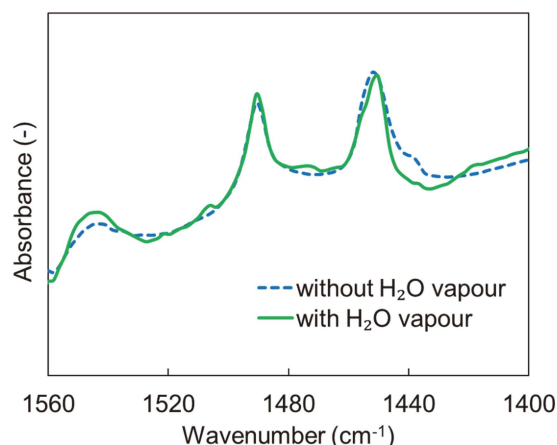


Fig. 5 FT-IR Spectra of Pyridine Adsorbed on Cu/HZSM-5 with and without Treatment with H_2O Vapour

Therefore, the acid nature of Cu/HZSM-5 may change with the calcination temperature.

FT-IR spectroscopy was performed, using pyridine as the probe. **Figure 4** shows the FT-IR spectra of pyridine adsorbed onto Cu/HZSM-5 calcined at different temperatures, and the peaks observed at 1450 cm^{-1} and 1540 cm^{-1} represent pyridine adsorbed on Lewis and Brønsted acid sites, respectively. The amount of adsorbed pyridine was determined using the area of each peak, and the acid quantity of each was calculated (Table S1)³⁵. With an increase in the calcination temperature, the intensities of the peaks at 1540 cm^{-1} and 1450 cm^{-1} respectively decrease and increase. This suggests that high-temperature calcination causes dehydration or -aluminum, which changes a Brønsted acid site to a Lewis acid site, as shown in **Scheme 1**. In the spectrum of Cu/HZSM-5 calcined at 773 K, two peaks are observed at approximately 1450 cm^{-1} , likely because pyridine adsorbs on Cu, which acts as a Lewis

acid site. However, confirming this assignment is challenging because the number of Lewis acid sites increases with increasing calcination temperature. Increasing the calcination temperature of Cu/HZSM-5 from 773 to 1273 K increases the number of Lewis acid sites. However, the fractions of this increase in the number of Lewis acid sites that can be attributed to framework and extra-framework Al are unclear. Therefore, pyridine adsorption FT-IR spectroscopy was performed after Cu/HZSM-5 encountered H_2O vapour. Framework Al loses its Lewis acid site and regenerates a Brønsted acid site when it encounters H_2O vapour^{36,37}, whereas extra-framework Al retains its Lewis acid site, even after encountering H_2O vapour. Therefore, these two types of Lewis acid sites can be distinguished by introducing H_2O vapour. **Figure 5** shows the pyridine adsorption FT-IR spectra with and without Treatment with H_2O vapour. Introducing H_2O vapour slightly decreases

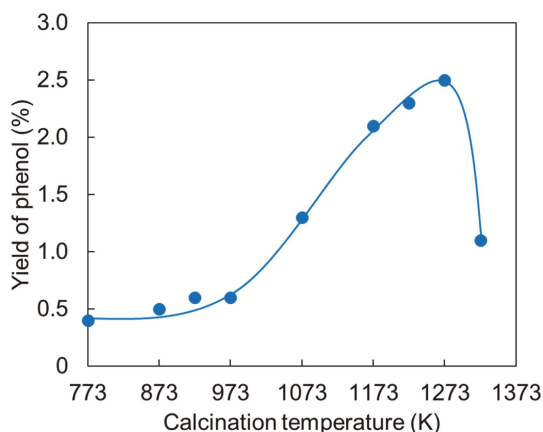


Fig. 6 Effect of the Calcination Temperature of Cu/HZSM-5 on the Phenol Yield upon Benzene Oxidation

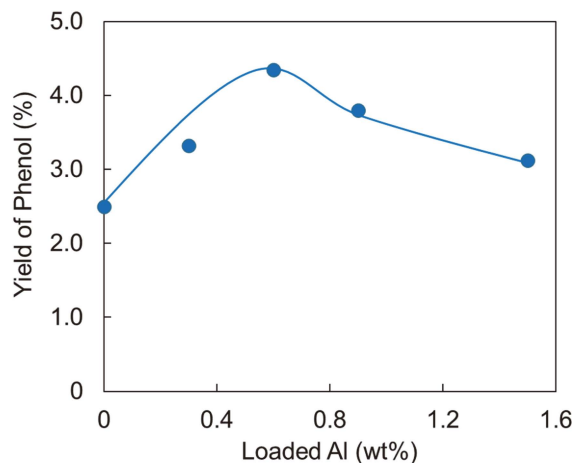


Fig. 8 Effect of the Al Loading on the Phenol Yield of Benzene Oxidation

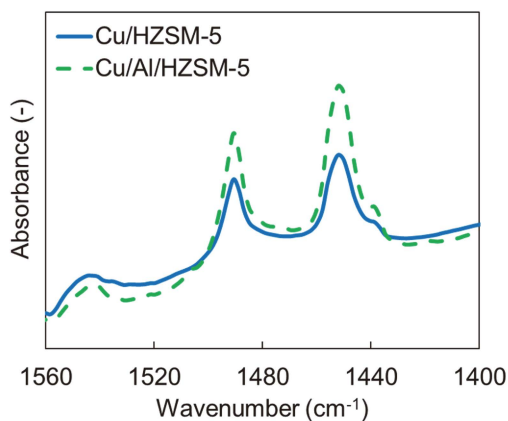


Fig. 7 FT-IR Spectra of Pyridine Adsorbed on Cu/HZSM-5 and Cu/Al/HZSM-5

es the area of the peak at 1450 cm^{-1} , whereas it slightly increases that of the peak at 1540 cm^{-1} . Hence, most of the increase in the number of Lewis acid sites upon high-temperature calcination of Cu/HZSM-5 can be attributed to extra-framework Al. Furthermore, the extra-framework Al may form as a five-coordinate Al species³⁸.

Figure 6 shows the relationship between the calcination temperature and phenol yield of Cu/HZSM-5, and the phenol yield increases with increasing calcination temperature. As the number of Lewis acid sites formed by extra-framework Al increases when Cu/HZSM-5 is calcined at a high temperature (1273 K), these Lewis acid sites may play a role in phenol formation via benzene oxidation. The phenol yield decreases when Cu/HZSM-5 calcined at $>1273\text{ K}$ is used, potentially because the catalyst cannot withstand calcination at 1323 K and its crystal structure collapses (Fig. S1, Table S3).

Table 1 BET Surface Areas of Cu/HZSM-5 and Cu/Al/HZSM-5(x) with Different Al Loadings

Catalyst	BET surface area [m^2/g]
Cu/HZSM-5	320
Cu/Al/HZSM-5(0.3)	316
Cu/Al/HZSM-5(0.6)	310
Cu/Al/HZSM-5(0.9)	309
Cu/Al-HZSM-5(1.5)	280

3. 2. Effect of Al Addition to Cu/HZSM-5

Cu/Al/HZSM-5 was prepared by loading Al and Cu onto HZSM-5 to increase the total amount of extra-framework Al within Cu/HZSM-5, which could contribute to phenol formation, and its acidic properties were investigated via pyridine adsorption FT-IR spectroscopy (**Fig. 7**). Al addition considerably increases the intensity of the peak attributed to pyridine coordinated to the Lewis acid sites, whereas almost no change is observed in the intensity of the peak attributed to pyridinium ions adsorbed on the Brønsted acid sites. This suggests that loaded Al functions as a Lewis acid site. Therefore, the effect of Al addition to Cu/HZSM-5 was investigated. **Figure 8** shows the yields of phenol obtained upon benzene oxidation over Cu/Al/HZSM-5 catalysts with different Al loadings, and Cu/Al/HZSM-5 affords higher phenol yields than those generated using Cu/HZSM-5, irrespective of the Al loading. The phenol yield increases upon increasing the Al loading to 0.6 wt%. At this point, the yields of all products increase, and thus, the conversion rate of benzene is improved. However, the phenol yield gradually decreases upon increasing the Al loading further. The BET surface area of the catalyst decreases upon increasing the amount of Al loaded (**Table 1**). At lower loadings, Al may be loaded as Al_2O_3 particles, but Al_2O_3 ag-

Table 2 Product Yields after Benzene Oxidation over Different Catalysts

Catalyst	Yields of products [%]			
	Phenol	Hydroquinone	<i>p</i> -Benzoquinone	CO _x
Cu/HZSM-5	2.5	0.24	0.58	6.4
Cu/Al/HZSM-5 (Al = 0.3 wt%)	3.3	0.41	0.98	5.8
Cu/Al/HZSM-5 (Al = 0.6 wt%)	4.2	0.60	1.70	6.7
Cu/Al/HZSM-5 (Al = 0.9 wt%)	3.5	0.55	1.30	6.4
Cu/Al/HZSM-5 (Al = 1.5 wt%)	3.1	0.59	1.50	7.9
Al/HZSM-5	0	0	0	2.3

Catalysts: Cu/HZSM-5 (calcined at 1273 K), Cu/Al/HZSM-5 (Al = 0.3-1.5 wt%), and Al/HZSM-5 (Al = 0.6 wt%).

Table 3 Product Yields after Benzene Oxidation over Cu/Silicalite and Cu/Al/Silicalite

Catalyst	Yields of products [%]	
	Phenol	CO _x
Cu/silicalite	0	6.6
Cu/Al/silicalite	0	6.9

Catalysts: Cu/silicalite and Cu/Al/silicalite (Al = 0.3 wt%).

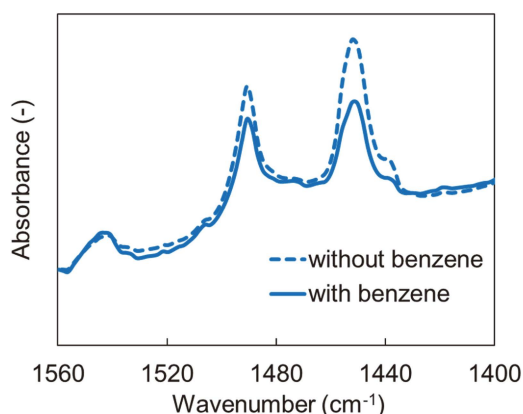
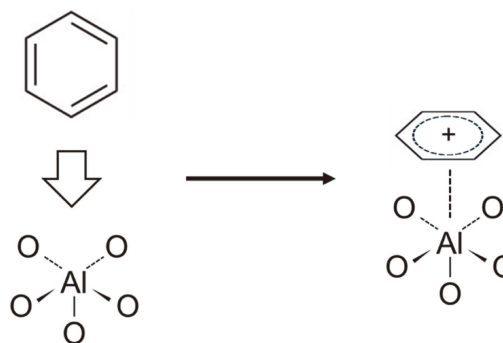


Fig. 9 FT-IR Spectra of Pyridine Adsorbed on Cu/Al/HZSM-5 with and without Benzene

gregates, which block the pores, thus decreasing the surface area, may form at higher loadings. Therefore, the decrease in the phenol yield due to excessive Al addition is likely caused by the blockage of the pores of the catalyst. Al/HZSM-5, wherein only Al is loaded onto HZSM-5, exhibits no catalytic activity in phenol formation (Table 2), suggesting that Al acts differently from Cu, which functions as an active species in phenol formation. Furthermore, the results obtained using silicalite, which is a support with the same pore structure as that of HZSM-5 but without framework Al, are shown in Table 3. Cu/silicalite and Cu/Al/silicalite, as prepared by loading Cu or Cu and Al onto silicalite, display no catalytic activity in phenol formation (Table 3). Therefore, the presence of framework Al is clearly essential in promoting the oxidation of ben-



Scheme 2 Interaction between Benzene and Extra-framework Al

zene to phenol in this reaction.

Pyridine adsorption FT-IR spectroscopy was performed using Cu/Al/HZSM-5 pre-adsorbed with benzene to investigate the contribution of extra-framework Al to benzene oxidation (Fig. 9). The intensity of the peak at 1450 cm⁻¹ decreases upon introducing benzene, and thus, the amount of pyridine adsorbed on the Lewis acid sites decreases. This suggests that benzene interacts with extra-framework Al, which serves as a Lewis acid site. Such an interaction may be caused by the attraction of the electron cloud of benzene to extra-framework Al, with an empty orbital (Scheme 2). Therefore, the extra-framework Al, functioning as a Lewis acid, may act as an adsorption site for benzene and promote the reaction.

3.3. Redox Behaviour of the Loaded Cu

An induction period has been observed during the gas-phase catalytic oxidation of benzene using O₂ and Cu/HZSM-5 as the oxidant and catalyst, respectively, until phenol is formed^{20,22)~24)}. Cu⁺ is crucial in phenol formation, although Cu also occurs in its divalent state immediately after loading, and thus, the induction period can be ascribed to the reduction of Cu²⁺ to Cu⁺. Therefore, the reaction was conducted using a catalyst pre-reduced with CO (Fig. 10). The induction period is no longer observed after the reduction treatment, suggesting that the induction period is attributable to the reduction of the Cu species.

PL spectroscopy was performed under various condi-

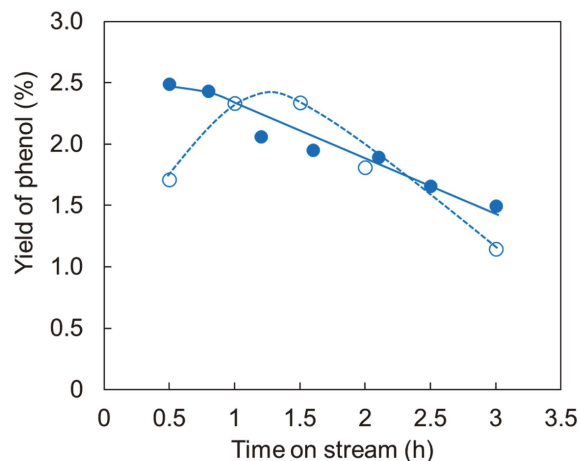


Fig. 10 Phenol Yields of Benzene Oxidation over Cu/HZSM-5 (open circles) and Pre-reduced Cu/HZSM-5 (filled circles) as Functions of Time on Stream

tions to further investigate the changes in the valence of Cu (**Fig. 11**). In the spectrum of Cu/HZSM-5, a PL peak attributed to Cu^+ is observed (~ 440 nm) immediately after reduction with CO (A)^{39,40}. After benzene oxidation over reduced Cu/HZSM-5 is conducted under the reaction conditions described in section 2.4, in situ measurement reveals a significant decrease in the intensity of the PL peak attributed to Cu^+ (B). This decrease is likely because of Cu^+ oxidation to Cu^{2+} in the presence of O_2 . Furthermore, when only inert N_2 gas and benzene are supplied to the reaction tube after the completion of the oxidation reaction, the intensity of the peak attributed to Cu^+ increases relative to that observed immediately after the oxidation reaction (C). Therefore, Cu^{2+} is reduced to Cu^+ by supplying only N_2 and benzene under the reaction conditions. Hence, Cu^{2+} may be reduced to Cu^+ by benzene and re-oxidised by O_2 during the reaction^{21,24}, and thus, benzene may be oxidised via the Cu redox cycle.

3.4. Suggested Reaction Mechanism

The loaded Cu initially occurs in its divalent state, but it is likely reduced to Cu^+ by benzene. Subsequently, O_2 is adsorbed onto Cu^+ , which is oxidised to Cu^{2+} , and furthermore, Cu^{2+} is reduced back to Cu^+ by benzene. The amount of CO adsorbed on Cu/Ti/HZSM-5 correlates with the amount of adsorbed O_2 ^{23,24}. As CO is selectively adsorbed onto monovalent Cu, O_2 is likely also adsorbed on Cu^+ ⁴¹. In addition, the O species adsorbed on the catalyst, rather than the O_2 in the gas phase, may be critical in phenol formation²¹. These findings suggest that O_2 is adsorbed onto Cu^+ , resulting in a reactive oxygen species that contributes to the formation of phenol from benzene. In contrast, the results of FT-IR spectroscopy suggest that benzene interacts with extra-framework Al (section 3.1), likely owing to the attraction of the electron

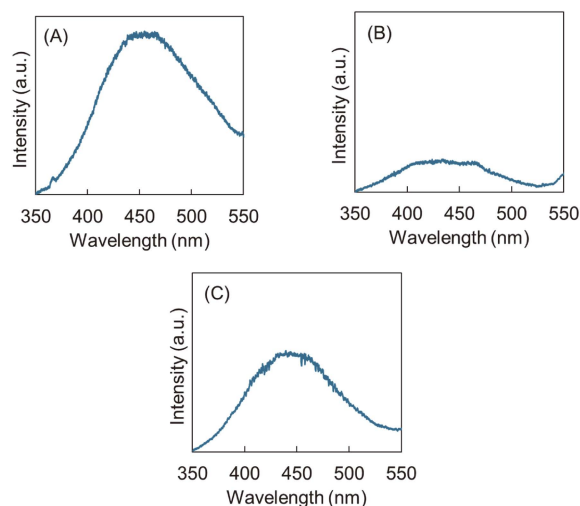
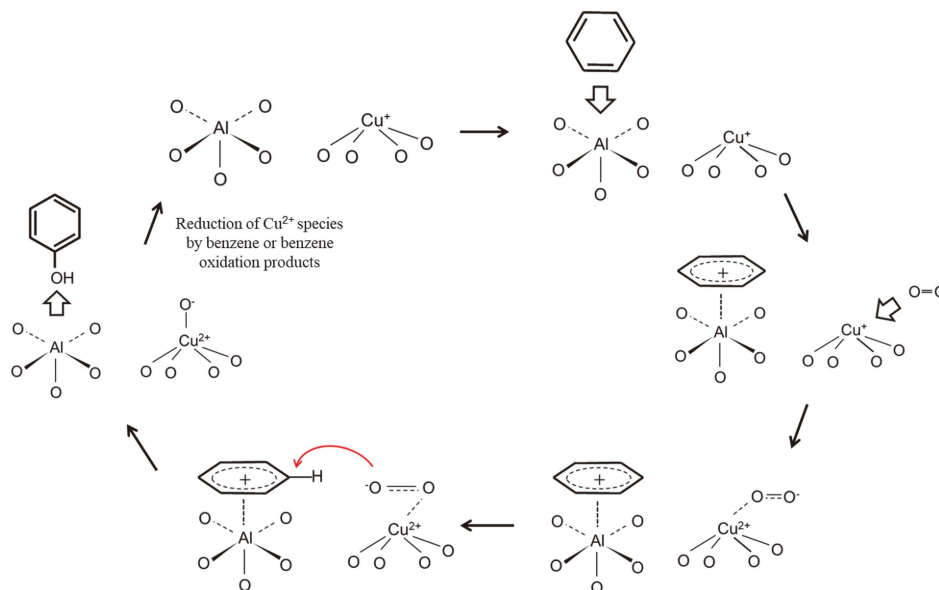


Fig. 11 PL Spectra of Cu/HZSM-5 Measured in situ under Various Conditions: (A) after reduction treatment with CO, (B) after benzene oxidation over pre-reduced Cu/HZSM-5 for 3 h, and (C) after supplying only N_2 and benzene for 1 h after the completion of benzene oxidation

cloud of benzene to extra-framework Al, which functions as a Lewis acid. Benzene interacting with extra-framework Al may decrease its electron density and yield δ^+ polarity. These results were used to propose the mechanism of phenol formation, as shown in **Scheme 3**. First, Cu^{2+} is reduced to Cu^+ by benzene, which then interacts with extra-framework Al. Subsequently, O_2 is adsorbed onto Cu^+ , which is oxidised to Cu^{2+} , and active oxygen species are generated. One O atom is then introduced into the benzene interacting with the extra-framework Al to form phenol, and the Cu^{2+} is again reduced by benzene.

4. Conclusions

The acidic properties of Cu/HZSM-5 in the gas-phase catalytic oxidation of benzene and the redox behaviour of Cu were investigated to determine the reaction mechanism. The calcination temperature of Cu/HZSM-5 significantly affected the phenol yield, with a higher catalytic activity in phenol formation observed with an increased calcination temperature. Pyridine adsorption FT-IR spectroscopy suggested that the Brønsted acid sites of Cu/HZSM-5 changed to Lewis acid sites upon calcination at a high temperature. Additionally, a large portion of the increased number of Lewis acid sites could be attributed to extra-framework Al produced via dealumination. Hence, the extra-framework Al, which functioned as a Lewis acid site, could contribute to phenol formation, and thus, we investigated the effect of Al addition on the content of extra-framework Al of Cu/HZSM-5 to further improve the phenol yield. The number of Lewis acid sites in-



Scheme 3 Mechanism of Phenol Formation

creased with Al addition, which enhanced the phenol yield. In addition, pyridine adsorption FT-IR spectroscopy of Cu/Al/HZSM-5 pre-adsorbed with benzene indicated that the peak intensity of pyridine adsorbed on the Lewis acid sites decreased. This suggested that benzene interacted with extra-framework Al, which functioned as a Lewis acid site, and thus, the extra-framework Al could be the site of benzene activation. Benzene was oxidised over Cu/HZSM-5 pre-reduced with CO, and the induction period before phenol formation was no longer observed, suggesting that this induction period was due to the reduction of Cu^{2+} to Cu^+ . The results of PL spectroscopy indicated that Cu^{2+} was reduced to Cu^+ by benzene, and the resulting Cu^+ was oxidised to Cu^{2+} by O_2 , which completed the redox cycle of Cu. Hence, extra-framework Al and Cu may act as activation sites for benzene and O_2 , respectively, suggesting that Cu/HZSM-5 functions as an effective binary catalyst that promotes phenol formation via benzene oxidation.

Supporting Information

Supplementary data associated with this article can be found in the online version at <https://jstage.jst.go.jp/browse/jpi/-char/en> (DOI: doi.org/10.1627/jpi.69.42).

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要 旨

Cu/HZSM-5触媒を用いたベンゼン気相接触酸化反応におけるフェノール生成活性とルイス酸点の関連性

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Cu/HZSM-5を触媒として用いたベンゼンの気相接触酸化反応を行い、フェノール生成機構の解明を試みた。Cu/HZSM-5触媒の焼成温度依存性を調べたところ、焼成温度の上昇に伴い、触媒のルイス酸サイトが増加し、フェノール生成活性も向上することが明らかとなった。これは、高温焼成により担体であるゼオライト中のアルミニウムが骨格外に移動し、形成した骨格外アルミニウムがルイス酸サイトとして機能することで、反応

基質であるベンゼンの吸着サイトとして作用し、フェノール収率の向上につながったものと考えられた。さらに、フォトルミネッセンススペクトルから、ゼオライト中のCu²⁺がベンゼンとの相互作用でCu⁺に還元され、酸素の吸着でCu²⁺に再酸化されるサイクルが示唆された。このCu種の酸化還元過程で生成した活性酸素種により、ルイス酸サイトに吸着したベンゼンが酸化され、フェノールが生成すると推測された。



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