



Selective catalytic oxidation of benzene over Cu/Ti/HZSM-5 under low oxygen pressure for one step synthesis of phenol



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ABSTRACT

The direct hydroxylation of benzene to phenol over a Cu impregnated zeolite catalyst (Cu/HZSM-5) is performed in airflow. Phenol is obtained as a main product in a yield of 2.5%, however, the selectivity of phenol is low (44.0%) due to the formation of by-products such as hydroquinone, *p*-benzoquinone, CO, and CO₂. The use of Cu/HZSM-5 leads to a significantly higher selectivity of phenol (94.0%) under an O₂ partial pressure that is lower than the atmospheric O₂ partial pressure. It is found that excess O₂ in the gas-phase causes the formation of by-products, whereas a decrease of O₂ partial pressure prevents the by-products from forming. Moreover, the addition of Ti to Cu/HZSM-5 leads to improved phenol formation activity. Good yield (4.3%) and selectivity (88.0%) of phenol are achieved over Cu/Ti/HZSM-5 under a low O₂ partial pressure. The addition of Ti is found to accelerate the formation of Cu⁺ as an active site. It is therefore speculated that phenol can be formed selectively over Cu/Ti/HZSM-5 under lower O₂ partial pressure owing to the increase of Cu⁺ sites by Ti addition and the prevention of by-product formation by the decreased O₂ partial pressure.

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1. Introduction

Catalytic partial oxidation reactions of hydrocarbons have important industrial applications. The oxidation of hydrocarbons has been widely studied for the manufacture of chemical derivatives such as alcohols, aldehydes, ketones, carboxylic acids, and epoxides, which are industrially significant [1–6]. Hence, their synthesis through an economical, low-energy, and green catalytic process is attractive and has been actively studied in the field of chemistry.

Phenol is one of the most important chemicals that find application in the fields of resins, fibres, and medicine. The current industrial process, the cumene process, has a 5% yield with 95% selectivity of phenol, and produces an equimolecular amount of acetone as a by-product. The cumene process is widely used in the chemical industrial field because of its high selectivity and a demand for acetone. However, the high-energy method requires a three-step reaction and distillation for the separation of the products and reactant. Therefore, the direct oxidation of benzene is an economically more desirable process for phenol

production without the formation of by-products. Many researchers have investigated the selective oxidation of benzene for the one-step synthesis of phenol. In particular, Panov et al. [7,8], Yoo et al. [9], Jia et al. [10], and Horváth et al. [11] have reported the catalytic gas phase oxidation of benzene to phenol over Fe supported catalysts with N₂O. They showed that 4.2% yield with >95% selectivity was achieved in the gas-phase hydroxylation of benzene with air-and-ammonia mixture over copper-based phosphate catalysts. Some researchers have reported the liquid-phase hydroxylation of benzene with TEMPO [12] or H₂O₂ [13–17]. Moreover, in terms of an environment-friendly and economical chemistry, there is a growing demand for catalytic oxidation of benzene employing a clean oxidant, that is, O₂ with few additives [18–23]. Although typical oxidants, such as N₂O, TEMPO, and H₂O₂, with additives give good yields, they are too expensive for practical purposes. Thus, the one-step synthesis of phenol from benzene without any additives is more desirable for industrial applications. We have studied the direct oxidation of benzene in the gas phase using only molecular O₂, which is an inexpensive oxidant. Cu impregnated on HZSM-5 has been found to catalyse the one-step synthesis of phenol from benzene and O₂ [24,25]. It has also been reported that the Cu/HZSM-5 catalyst with TiO₂ added (Cu/Ti/HZSM-5) improves phenol formation [25]. However, the obtained selectivity of phenol is quite low (>40% [25]) due

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to by-products formed by the excess oxidation of benzene and phenol to CO and CO₂. In the present paper, we attempt to improve the selectivity of phenol over Cu/Ti/HZSM-5 by adding Ti to the catalyst and changing the reaction gas composition. The effects of Ti addition and the Ti/Cu ratio on the catalytic performance are also described in detail by means of O₂ uptake measurements.

2. Experimental

2.1. Materials

All materials were obtained commercially. The HZSM-5 (Si/Al atomic ratio=29) zeolite was purchased from ZEOLIST. Cu(OAc)₂·H₂O, [TiO(C₂O₄)₂]*n*H₂O, benzene, toluene, and 2-propanol were purchased from Nacalai Tesque. All the chemicals were used without any further purification.

2.2. Catalyst preparation

Cu impregnated on HZSM-5 (Cu/HZSM-5) catalyst was prepared by an impregnation method according to the previous report [26] as follows. HZSM-5 zeolite (0.10 g) was substantially dispersed in 50 mL of distilled water with the selected amount of Cu(OAc)₂·H₂O (Nacalai Tesque), corresponding to the desired amount of Cu oxide loading. The mixture was evaporated at 343 K in vacuum. The obtained solid was dried at 393 K overnight, and then calcined under airflow at 1273 K for 5 h. The samples were designated as Cu/HZSM-5 and contained 0.70 wt% of Cu.

Cu and Ti supported HZSM-5 (Cu/Ti/HZSM-5) catalysts were prepared by an impregnation method as follows. TiO(C₂O₄)₂·*n*H₂O

$$\text{Selectivity of phenol (\%)} = \frac{\text{mole number of phenol}}{\text{total mole number of [phenol, hydroquinone, and } p\text{-benzoquinone] and } 1/6 \times [\text{CO}_2]} \times 100$$

(Nacalai Tesque) as the source of Ti and HZSM-5 were added to distilled water, dispersed, and evaporated in vacuum. The obtained solid was dried at 393 K overnight, and then calcined under airflow at 773 K for 5 h. The obtained Ti/HZSM-5 was mixed with Cu(OAc)₂·H₂O in distilled water, evaporated in vacuum, and then dried at 393 K. The obtained solid was calcined under airflow at 1273 K for 5 h. The samples were composed of 0.70 wt% Cu and 0.26–0.74 wt% Ti (Ti/Cu atomic ratio = 0.5–1.4).

2.3. Gas-phase catalytic oxidation of benzene in a flow reactor

The direct oxidation of benzene in gas-phase was performed using a conventional continuous flow system with a fixed-bed pyrex glass reactor (internal diameter = 18 mm) at atmospheric pressure. The catalyst was calcined at 773 K for 2 h under airflow and purged with N₂ gas for 30 min at 773 K before the reaction. The reaction conditions were as follows: *W* (catalyst weight) = 0.5 g; *F* (total flow rate) = 2.12 × 10⁻³ mol/min; *W/F* = 2.36 × 10² g-cat/min/mol; reaction temperature = 673 K; benzene partial pressure = 3.75 kPa; O₂ partial pressure = 1.27–20.26 kPa; and balance gas = N₂. The reaction products were trapped at 223 K using a refrigerant (liquid nitrogen + diethyl malonate) until benzene, which is highly carcinogenic, is completely removed and dissolved in a mixture of toluene and 2-propanol (1:1 v/v). The products (phenol, hydroquinone, and *p*-benzoquinone) were analysed with a high performance liquid chromatograph (Jasco, LC-2000 Plus) equipped with a C18 column using a mixed solution carrier of 0.1 vol% phosphoric acid aqueous solution and acetonitrile (1:1 v/v). The gaseous products, such as CO and CO₂, were analysed with a gas chromatograph equipped with a thermal conductivity detector (TCD) using stainless steel columns containing active carbon (1 m) and molecular sieves 13X (3 m) at 323 K under H₂ carrier. Yields of phenol,

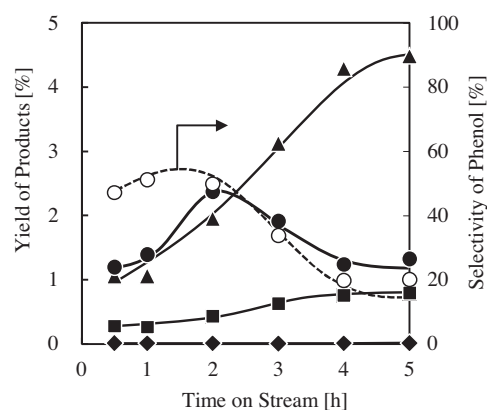


Fig. 1. Time profiles of the product yields for the oxidation of benzene over Cu/HZSM-5 catalyst (Cu = 0.7 wt%, Si/Al = 29). Total pressure = 101.32 kPa (N₂:O₂:benzene = 4:1:0.18); yield of phenol (●), hydroquinone (◆), *p*-benzoquinone (■), and CO_x (▲); selectivity of phenol (○).

hydroquinone, *p*-benzoquinone, CO, or CO₂, and the selectivity of phenol were calculated using the following equation:

Yields of phenol, hydroquinone, and *p*-benzoquinone (%)

$$= \frac{\text{mole number of each product}}{\text{mole number of benzene fed}} \times 100$$

$$\text{Yield of CO}_x (\%) = \frac{1/6 \times \text{mole number of [CO and CO}_2\text{]}}{\text{mole number of benzene fed}} \times 100$$

2.4. Characterisation

The photoluminescence spectra of Cu/HZSM-5 were recorded using a fluorescence spectrophotometer (F-7000, HITACHI) with a Xenon lamp as the excitation light source at 73 K in vacuum. The fluorescence was generated by continuous-wave, near-UV excitation at 280 nm.

The O₂ uptake on the surface of the catalyst was measured using a constant-volume-type semi-micro gas-adsorption apparatus connected to a quartz cell in which the catalyst was charged. The catalyst was calcined under an O₂ atmosphere at 773 K for 1 h. After calcination, the catalyst was evacuated at 773 K for 1 h, and then reduced under a CO atmosphere at 773 K for 1 h. The dead volume in the cell at 673 K was measured by charging 1.3 kPa of He gas. The total uptake of O₂ was measured after O₂ adsorption equilibrium under 2.6 kPa of O₂ at 673 K. After the evacuation at 673 K for 1 h, the reversible adsorbed uptake of O₂ was measured by charging 2.6 kPa of O₂. The calculated irreversible uptake of O₂ could be defined as the amount of O₂ that is selectively adsorbed on the Cu surface of catalyst [13]. The amount of Cu⁺ sites was estimated by the O₂ uptake measurement.

3. Results and discussion

3.1. The catalytic test of Cu/HZSM-5

The benzene oxidation reaction was performed over Cu/HZSM-5 at 673 K under airflow (mole ratio N₂:O₂:benzene = 4:1:0.18). The time profiles of the product yields and phenol selectivity are shown in Fig. 1. The yield of phenol increases over time and attains a maximum yield of 2.3% within 2 h. The selectivity of phenol is 48.0% at 2 h. When the reaction time is prolonged beyond 5 h, the yield and

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