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

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Introduction

Phenol is an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics. Many attempts have been made to find a way to one-step synthesis of phenol from benzene instead of the cumene process. We have reported that copper supported on HZSM-5 catalysts calcined at high temperature are active for the gas-phase catalytic oxidation of benzene to phenol [1-3]. In this study we investigate the effect of titanium addition to Cu/HZSM-5.

Experimental

HZSM-5 was obtained commercially (ZEOLYST: Si/Al = 29). Ti/HZSM-5 was obtained by an impregnation with an aqueous solution of $[TiO(C_2O_4)_2]•nH_2O$. Cu/HZSM-5 and Cu/Ti/HZSM-5 were prepared by an impregnation method using an aqueous solution of $Cu(CH_3COO)_2•H_2O$. After impregnation, the catalyst was dried at 393 K overnight, then calcined at 1273 K in air flow for 5 h. After impregnation, the catalyst was dried at 393 K overnight, then calcined at 773 K for 5 h in air flow. The oxidation of benzene was carried out using a fixed bed flow reactor. The products were analyzed by Liquid chromatograph and Gas chromatograph.

Results/Discussion

Cu/HZSM-5 and Cu/Ti/HZSM-5 catalysts oxidized benzene to phenol, hydroquinone, p-benzoquinone, CO, and CO2. Titanium addition to Cu/HZSM-5 catalyst caused the increase of phenol yield. In this case, the selectivity of phenol formation also improved by the Ti addition to Cu/HZSM-5. Figure 1 indicates the dependence of the amounts of titanium addition to Cu/HZSM-5 catalysts. 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, CO_2 yield continuously increases with the increase of Ti/Cu atomic ratio. It is speculated that the active site of CO_2 formation is different from that of phenol, hydroquinone and p-benzoquinone. We previously reported that Cu^+ species on the zeolite played an important role for phenol formation in the gas-phase direct oxidation of benzene [1]. It was considered that the redox cycle of Cu^+ and Cu^{2+} caused the partial oxidation of benzene. ESR measurements were also shown that the Ti addition to Cu/ HZSM-5 could be easily reduced in comparison with Cu/HZSM-5. 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 partial oxidation products effectively.

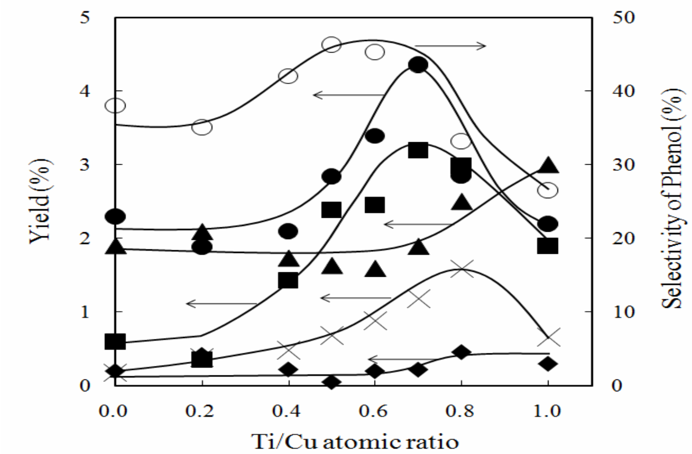

Figure 1. Dipendence of the Ti/Cu atomic ratio of Cu/Ti/HZSM-5 catalysts on the benzene oxidation. Catalyst, Cu/Ti/HZSM-5 (Cu = 0.7 wt%, Ti/Cu = 0 – 1.0, Si/Al = 29) ; Yield of phenol (●) , hydroquinone (×), p-benzoquinone (■), CO (♦) and CO_2 (▲) : Selectivity of phenol (○).

References.

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