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CATALYTIC REACTION MECHANISMS

Partial Gas-Phase Oxidation of Toluene by the Heteropoly Acid $H_4PMo_{11}VO_{40}$ Supported on ShAS-2 Aluminosilicate

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Abstract—The effects of reaction conditions and concentration of the heteropoly acid $H_4PMo_{11}VO_{40}$ supported onto ShAS-2 bead aluminosilicate on the conversion of toluene into benzoic acid in the partial oxidation of toluene by atmospheric oxygen were studied. The results demonstrated that the conversion of toluene was an extremal function of temperature, space velocity (v), and toluene concentration (C_0) in the initial air mixture. An increase in the heteropoly acid concentration from 2 to 30% increased the conversion of toluene into benzoic acid in the partial oxidation of toluene from 1.5 to 12.6% at optimum process parameters: T = 300°C, v = 2000 h^{-1}, and C_0 = 13.72 g/m^3.

INTRODUCTION

It is well known that catalysts for the conversion of aromatic hydrocarbons should exhibit the properties of solid acids. According to published data [1, 2], heteropoly acids are strong protic acids, which are stronger than ordinary mineral and solid acids (H_2SO_4, Al_2O_3–SiO_2), and efficient catalysts for basic and fine organic synthesis [3]. Thus, in the synthesis of vitamins (such as vitamins E and C and other) and diethyl ether, heteropoly acids exhibit higher activity than that of commonly used ordinary catalysts [4, 5].

The aim of this work was to study the effect of a heteropoly acid ($H_4PMo_{11}VO_{40}$ HPA) on the conversion of toluene into benzoic acid in the partial oxidation of toluene by atmospheric oxygen on ShAS-2 bead aluminosilicate.

EXPERIMENTAL

The catalysts were prepared by the impregnation of ShAS-2 bead aluminosilicate (specific surface area S_{sp} = 340 m^2/g and d = 3–4 mm) with an aqueous solution of the heteropoly acid $H_4PMo_{11}VO_{40}$.

The experiments were performed in a flow unit at atmospheric pressure (catalyst sample weight of 2.5 g) over the temperature range 200–350°C at space velocities (v) of 500–3000 h^{-1} and at toluene concentrations (C_0) in the initial air system equal to 13.72–385 g/m^3.

Chromatographic analysis was used for determining the concentrations of initial and unreacted toluene (a column (l = 1.5 m; d = 4 mm) with 15% Apiezon L on Chromaton N-AW), toluene oxidation products (benzoic acid, benzaldehyde, etc.) [6, 7], CO, and CO_2.

In addition, benzoic acid was determined by titration with a 0.1 N NaOH solution in accordance with *GOST* (State Standard) *10521-78.*

RESULTS AND DISCUSSION

In the first series of experiments, we studied the effects of temperature, space velocity, and toluene concentration in the initial air mixture on the conversion of toluene into benzoic acid in the reaction of partial toluene oxidation by atmospheric oxygen on a 15% HPA/ShAS-2 catalyst. Table 1 summarizes the results. It can be seen that the conversion of toluene into benzoic acid passed through a maximum as the space velocity was increased from 500 to 2000 h^{-1} at 200–400°C. A maximum toluene conversion (3.89%) over the range v = 500–1500 h^{-1} was observed at 200°C. As the space velocity was increased to 2000 h^{-1}, the conversion of toluene into benzoic acid was as high as 6.00% at T = 300°C. A further increase in the reaction temperature and space velocity resulted in a dramatic decrease in the conversion of toluene into benzoic acid (to 1.84%). As the initial concentration of toluene in the

Table 1. Effects of temperature and space velocity on the conversion (α) of toluene into benzoic acid in the partial oxidation of toluene by atmospheric air on a 15% HPA/ShAS-2 catalyst

T, °C	α, %			
	500 h^{-1}	1000 h^{-1}	1500 h^{-1}	2000 h^{-1}
170	1.65	2.06	1.97	–
200	2.06	2.75	3.89	3.70
250	1.97	2.30	3.52	4.90
300	1.70	1.97	3.02	6.00
350	1.65	1.42	1.97	2.30
400	0.78	1.37	1.65	1.84

Note: Reaction conditions: C_0(toluene) = 20.59 g/m^3; catalyst weight, 2.5 g.

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Table 2. Effect of heteropoly acid concentration on the conversion (α) of toluene into benzoic acid in the partial oxidation of toluene by atmospheric air on HPA/ShAS-2 catalysts

T, °C	α, %		
	2% HPA/ShAS-2	15% HPA/ShAS-2	30% HPA/ShAS-2
200	1.68	5.46	7.90
250	–	6.55	10.10
300	1.50	7.56	12.60
350	–	5.80	7.10
400	1.40	4.10	–

Note: Reaction conditions: $v = 2000\ h^{-1}$; C_0(toluene) = 13.72 g/m^3.

starting mixture with air was increased, the conversion of toluene into benzoic acid at 200°C and 1500 h^{-1} noticeably decreased (3.89, 3.74, 1.23, and 0.83% at 20.59, 27.59, 85.30, and 385 g/m^3, respectively). At optimum parameters (T = 300°C, v = 2000 h^{-1}, and C_0 = 13.72 g/m^3), the conversion of toluene into benzoic acid was as high as 7.56%.

The heteropoly acid concentration on ShAS-2 aluminosilicate had a considerable effect on the conversion of toluene into benzoic acid in the reaction of partial toluene oxidation by atmospheric oxygen.

Table 2 summarizes data on the effect of heteropoly acid concentration on the conversion of toluene into benzoic acid at optimum parameters: v = 2000 h^{-1} and C_0 = 13.72 g/m^3). As can be seen in Table 2, an increase in the heteropoly acid concentration on ShAS-2 aluminosilicate up to 30% significantly increased the conversion of toluene. The highest toluene conversion (12.60%) was observed at 300°C on 30% HPA/ShAS-2, whereas the lowest conversion (1.5%) was observed on 2% HPA/ShAS-2.

According to chromatographic analysis data, benzoic acid was the only product of partial toluene oxidation by atmospheric oxygen on HPA/ShAS-2 catalysts at optimum parameters (300°C, 2000 h^{-1}). At higher temperatures (above 300°C), trace benzaldehyde and an insignificant amount of CO_2 were detected along with benzoic acid.

A comparison of the results with published data demonstrated that the conversion of toluene into benzoic acid on heteropoly acids supported on ShAS-2 was almost two times higher than that on V_2O_5 or V_2O_5–K_2SO_4–SiO_2, where toluene conversion did not exceed 6.0–6.9% [8, 9].

Thus, we found that heteropoly acids can be used in the partial oxidation reactions of aromatic hydrocarbons (such as toluene).

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