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Cyclodehydration of 1,4-butanediol to tetrahydrofuran catalyzed by supported silicotungstic acid

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Abstract

Acid strength, acid density, and the combination ability between silicotungstic acid and support were investigated when supported silicotungstic acid was used as a catalyst for cyclodehydration of 1,4-butanediol to tetrahydrofuran. The interaction between heteropoly acid and support influenced the catalytic activity. TiO_2-supported silicotungstic acid catalyst exhibited high activity when compared to the other catalysts supported by kaolin, kieselguhr, and activated charcoal.

Keywords: 1,4-Butanediol; Tetrahydrofuran; Heteropoly acid; Cyclodehydration

1. Introduction

Protonic mineral acids, such as H_2SO_4, HF, H_3PO_4, HNO_3, and $HClO_4$, are conventionally used as homogeneous catalysts in many industrial reactions. Although these homogeneous catalysts have many advantages, such as high activity and selectivity, they are corrosive, toxic, and difficult to separate from reaction solution [1,2]. Eco-friendly green approach has lately been expanded leading to the development of increasingly clean chemical procedures, such as supported acid catalysis and microwave-assisted catalysis [3]. Supported heteropoly acids have been pointed lately as versatile green catalysts for a variety of reactions, such as esterification [4], alkylation of aromatics [5,6], isomerization of *n*-alkanes [7,8], dehydration of ethanol [9], hydration of ethylene [9], and cyclodehydration of 1,4-butanediol [10,11].

Catalytic synthesis of tetrahydrofuran from maleic anhydride or its derivatives, such as 1,4-butanediol, has attracted a great deal of attention in point of view of economical and environmental benignancy [10–14]. The cyclodehydration of 1,4-butanediol to tetrahydrofuran catalyzed by heteropoly acids (tungstophosphoric acid, silicotungstic acid, and molybdophosphoric acid) supported on alumina, Y-, β-, and ZSM-5 zeolites exhibits high activity and selectivity [10,11]. The interaction between heteropoly acid and various kinds of supports should result in different catalytic activity.

In the present work, we studied the structure, acid strength, and acid density (concentration) of the kaolin-, titanium dioxide-, kieselguhr-, and activated charcoal-supported silicotungstic acid catalysts, and the combination degree between silicotungstic acid and the above-mentioned supports. The catalytic activity of the supported catalyst in cyclodehydration of 1,4-butanediol was relative to the silicotungstic acid loading, the type of support, and the calcination temperatures in preparation of the supported catalyst.

2. Experimental

2.1. Catalyst preparation

A series of silicotungstic acid (HWSi) catalysts with different HWSi loadings (5, 15, and 25 wt%) supported by

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kaolin (110 m^2/g), TiO_2 (50 m^2/g), kieselguhr (15 m^2/g), and activated charcoal (1000 m^2/g), respectively, were prepared by incipient wetness method. After impregnation, the as prepared catalysts were calcined at 120, 180, and 220 °C, respectively, for 4 h.

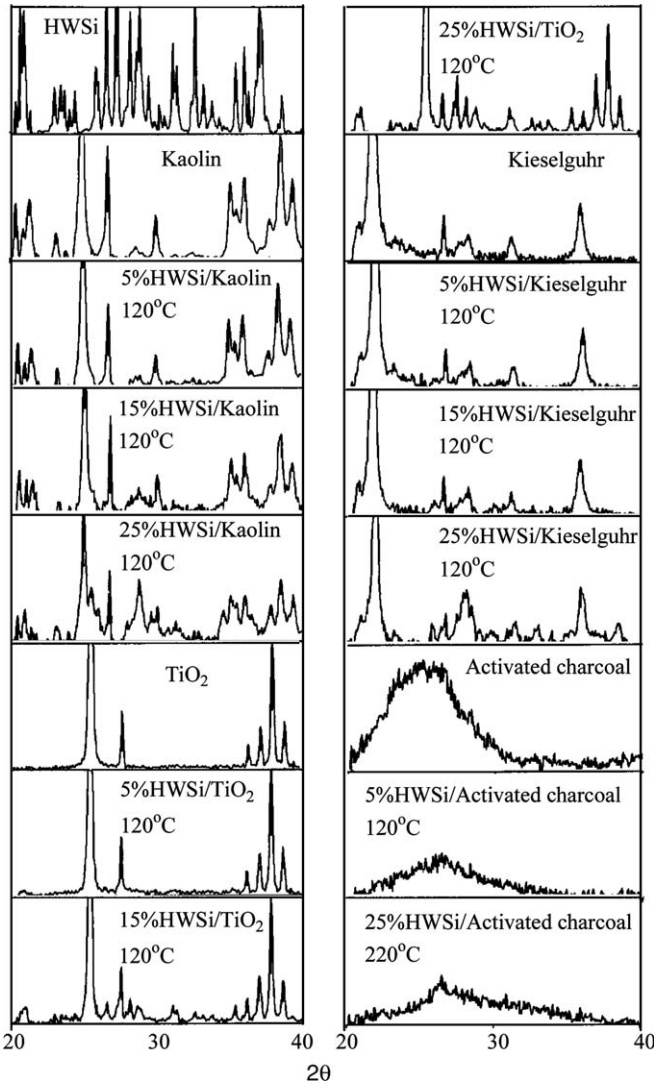

Fig. 1. XRD patterns of silicotungstic acid, kaolin, kieselguhr, TiO_2, activated charcoal, and representative supported silicotungstic acid catalysts prepared under different conditions.

2.2. Catalyst characterization

All supported HWSi catalysts were analyzed with a Shimada DX-D1 powder diffractometer using Kα radiation at 30 kV and 30 mA. The representative XRD patterns of the supported HWSi catalysts are shown in Fig. 1.

The combination degree of HWSi with support was determined by a desorption experiment of a supported HWSi catalyst in distilled water. A 25 ml of aqueous solution containing 0.5 g of catalyst was stirred at 25 °C for 1 h. The amount of the desorbed HWSi in the filtrate was analyzed by titration method using a 0.01 mol/L NaOH solution. HWSi desorption ratio was calculated by dividing the amount of the desorbed HWSi by the initial amount of HWSi in the catalyst. The results of HWSi desorption from the supported HWSi catalysts are listed in Table 1.

The acid strength and acid density of the supported HWSi catalyst were analyzed by acid–base titration

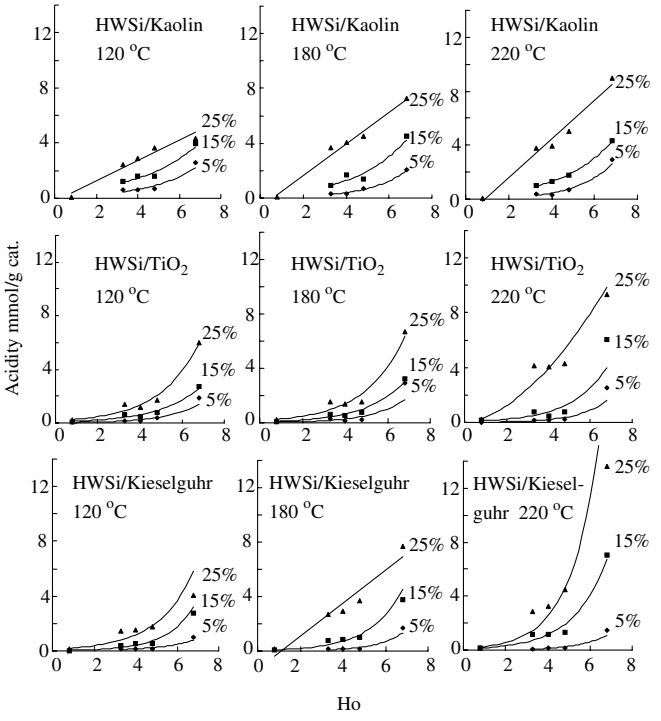

Fig. 2. The acid density and strength of supported silicotungstic acid catalyst prepared with different silicotungstic acid loading and under different calcination temperature.

Table 1
Silicotungstic acid desorption ratios of the catalysts

Catalysts	Desorption ratios % at different calcination temperature (°C)			Catalysts	Desorption ratios % at different calcination temperature (°C)		
	120	180	220		120	180	220
5%HWSi/Kaolin	64.1	70.7	65.8	5%HWSi/Kieselguhr	0	12.3	16.4
15%HWSi/Kaolin	59.8	73.3	78.8	15%HWSi/Kieselguhr	9.5	54.3	65.2
25%HWSi/Kaolin	82.2	78.1	82.2	25%HWSi/Kieselguhr	41.1	69.1	74.0
5%HWSi/TiO_2	49.3	65.8	57.6	5%HWSi/Activated charcoal	16.4	16.8	17.8
15%HWSi/TiO_2	70.7	81.5	84.5				
25%HWSi/TiO_2	87.2	90.4	89.2	25%HWSi/Activated charcoal	17.0	23.0	26.3