티타늄을 함유한 탄소-실리카 복합 에폭시화 촉매의 제조 및 촉매적 활성

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Synthesis of titanium containing carbon silica composite epoxidation catalysts and their catalytic activity

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Introduction

The importance of epoxide is understood by the fact that it accounts for more than one million tons annual production of propylene oxide and increasing needs for epoxde products from olefins worldwide. Therefore, the epoxidation reactions have attracted considerable attention. The most well known example is the catalytic epoxidation of olefins with H_2O_2 over titanium containing catalysts [1~4]. A heterogeneous Ti(IV)/silica catalyst for epoxidation of alkenes has been extensively studied from the end of 80's. These Ti(IV)/silica catalysts show a good catalytic activity with large molecules using organic hydroperoxide as the oxidant. However, they show a relatively low epoxide selectivity if hydrogen peroxide is used as the oxidant due to the hydrophilic nature of surface.

In recent years, surface modification of Ti(IV)/silica catalysts has received much attention as one way to obtain high yield of epoxide. For example, the silylation technique for the modification of silica surface was reported by several research groups [5~10]. The silylation method, however, cannot completely eliminate the hydrophilic nature of the silica surface in titanium containing catalysts, because the hydrophobic moieties may suffer from solvolysis with polar solvent under certain conditions [11, 12]. In our previous work, we used activated carbon as catalyst support to modify titanium catalyst and observed an increased epoxidation activity. Especially, carbon has hydrophobic surface property, so one can suppress the side reactions occurring over hydrophilic silica surface. On the other hand, the acidic properties of activated carbon give rise to the formation of byproducts.

In this study, it is aimed to report a simple and effective synthesis method of titanium containing carbon-silica composite catalyst and examine whether these catalysts may yield a better epoxide selectivity in the liquid phase epoxidation of cyclohexene. For this purpose, the catalysts were prepared by surface coating method using tetraethyl orthosilicate (TEOS) as silica source and also by surface grafting method, and applied to the epoxidation of cyclohexene with tert-butyl hydroperoxide (TBHP) and H_2O_2, respectively. We further synthesized the titanium grafted amorphous silica and Ti-MCM-41 to compare the catalytic performance with the titanium loaded carbon-silica composite catalysts.

Experimental

Preparation of catalysts

The titanium containing catalysts were prepared by the post synthesis method with activated carbon (Darco KB-B) and carbon-silica composite as supports. The activated carbon was washed and dried before use. The synthesis of carbon-silica composite was carried out with various ratios of TEOS/Ethanol. The TEOS/Ethanol solution was stirred for 3 h to allow TEOS to diffuse to the surface of carbon. Then distilled water was added in the amount of 5 wt% of TEOS to hydrolyze the TEOS. After stirring for 72 h, the carbon-silica composite was thoroughlywashed with ethanol to remove the residual TEOS, filtered off and dried at 383 K for 12 h.

All the titanium containing catalysts were synthesized by the post synthesis method with titanium alkoxide as the titanium source. The $Ti(OiPr)_4$ (titanium isopropoxide: Kanto Chemical) was dispersed in n-hexane under dry N_2. The support (activated carbon or carbon-silica composite) was dried and added to the solution. This was stirred at room temperature for 3 h. The solid obtained was filtered off, thoroughly washed with solvent to remove unreacted $Ti(OiPr)_4$ and subsequently dried at 383 K for 24 h. For the purpose of comparison, Ti-MCM-41 was synthesized using the procedure reported in the reference [13] and Ti containing amorphous silica (Sigma, average pore size 60 Å) was prepared by the same method as for the synthesis of carbon catalysts. All the catalysts prepared are listed in Table 1.

Table 1. Titanium containing catalysts prepared in this work.

catalyst	synthesis method	Ti-source
Ti-silica	Titanium grafted on amorphous silica	$Ti(OiPr)_4$
Ti-MCM-41	Hydrothermal synthesis	$Ti(OiPr)_4$
Ti-carbon	Fresh carbon (Darco KB-B)	$Ti(OiPr)_4$
Ti-carbon silica A	TEOS : EtOH = 50:50 composite	$Ti(OiPr)_4$
Ti-carbon silica B	TEOS : EtOH = 70:30 composite	$Ti(OiPr)_4$
Ti-carbon silica C	TEOS : EtOH = 90:10 composite	$Ti(OiPr)_4$
Ti-carbon silica D	TEOS : EtOH = 100:0 composite	$Ti(OiPr)_4$

Characterization of catalysts

The concentration of functional groups on the carbon surface was determined by the Boehm's titration method [14]. The contents of silica and titanium of carbon-supported catalysts were measured by ICP using Shimadzu ICPQ 1000spectrometer. The Ti-MCM-41 and titanium grafted silica were identified by FT-IR and UV-vis [15~17].

Epoxidation of cyclohexene

In a typical procedure, 100 mg of catalyst and 20 mmol of cyclohexene were taken and put into 20 ml of acetonitrile. After the reaction mixture was heated to 343 K under stirring, 10 mmol of TBHP (70 % in water) or H_2O_2(30 % in water) was introduced in one lot. The reaction was monitored by gas chromatography equipped with HP-5 capillary column and FID detector using cyclohexane as the internal standard.

Results and discussion

Preparation of catalysts

The surface nature of activated carbon was analyzed by the Boehm's titration method and the surface area of catalyst support was measured by the BET analysis. According to these analysis, the activated carbon has a large surface area and has good surface properties as a support for catalysts for grafting reaction. In the case of carbon-silica composites, the surface area tends to decrease as the silica content increases. These materials, however, have still sufficient surface areas for use as catalyst support.

Figure 1 presents the contents of Si and Ti in the carbon-silica composites. The Ti-carbon catalyst has less than 6 wt% of Ti, which is larger than the amount needed to saturate all the functional groups of the activated carbon used. The total amount of functional groups is ca. 0.63 mmol/g. If all the functional groups react with $Ti(OiPr)_4$, the activated carbon would contain almost 3 wt% titanium. Since the titanium grafting reaction was performed under anhydrous condition, the hydrolysis of $Ti(OiPr)_4$ could not occur. Therefore, it is evident that the loading of Ti took place in a similar manner to the case of titanium grafting on silica support [16~17].

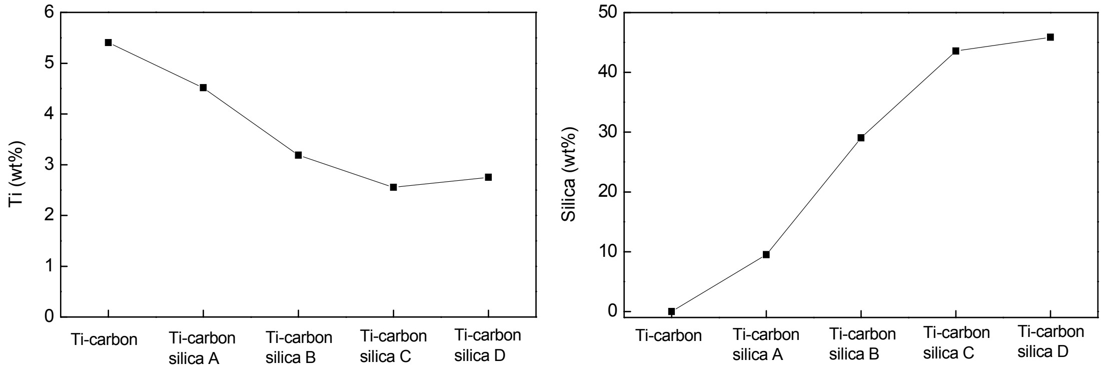

Figure 1. Contents of titanium and silica in the catalysts

According to Figure 1, the content of titanium loaded on the carbon-silica composite is affected by the amount of silica loaded on the carbon surface. Since the silica network is formed on the surface of activated carbon, the surface area of carbon-silica composite is decreased with the amount of silica loaded on the activated carbon. Therefore, the amount of titanium introduced in the carbon-silica composite is decreased with the silica loading.

Table 3. Results of cyclohexene epoxidation using TBHP and H_2O_2, respectively, as the oxidant.

catalyst	Oxidant	Yeild of epoxde	Selectivity		
			Epoxide	diol	1-ol +1-one
Ti-silica	TBHP	17.4	84.8	10.0	5.2
	H_2O_2	1.4	11.3	52.4	36.3
Ti-MCM-41	TBHP	16.5	90.0	5.9	4.1
	H_2O_2	2.8	16.2	54.9	28.9
Ti-carbon	TBHP	5.6	95.7	1.7	2.6
	H_2O_2	1.9	30.5	34.4	35.1
Ti-carbon silica A	TBHP	9.0	85.6	3.5	10.9
	H_2O_2	2.4	40.7	56.9	2.5
Ti-carbon silica B	TBHP	12.5	95.6	1.9	2.5
	H_2O_2	4.8	67.6	25.5	6.8
Ti-carbon silica C	TBHP	12.1	96.3	1.2	2.5
	H_2O_2	4.1	66.2	12.2	21.5
Ti-carbon silica D	TBHP	9.0	89.8	1.7	8.5
	H_2O_2	3.7	70.0	17.8	12.2

Cyclohexene epoxidation over various catalysts

The results of cyclohexene epoxidation presented in Table 2 show that the catalytic performance is significantly improved when the carbon-silica composites were used as the catalyst support. For both oxidants, the conversion of cyclohexene was increased by using the carbon-silica composites as support. Moreover, when H_2O_2 was used as the oxidant, the composite based catalysts show a much better epoxide selectivity than Ti-carbon catalyst and the yield of epoxide increased to almost twice of that over the silica-based catalysts.

It seems evident that the carbon-silica composite catalysts have characteristic advantages of the two different catalyst supports; one is the hydrophobic surface of the activated carbon and the other is the local environment of active titanium catalytic center on the silica support.

Conclusions

The carbon-silica composite material was found to be a good support for the titanium containing catalysts. Ti could be loaded successfully on the carbon-silica composite by the post synthesis method. The carbon-silica composite catalyst showed a high conversion and selectivity to epoxide compared to Ti-carbon catalyst and silica based catalysts for the cyclohexene epoxidation with H_2O_2. The highest values of cyclohexene conversion and epoxide selectivity were obtained with the carbon-silica composite catalyst having a titanium content of 3 wt%.

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