Preparation of titanium-containing carbon–silica composite catalysts and their liquid-phase epoxidation activity

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Titanium-containing catalysts have been prepared by two different post-synthesis methods using activated carbon and carbon–silica composite as catalyst supports. They have been applied to the liquid-phase epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP) and H_2O_2. The carbon–silica composite catalyst showed a high conversion and selectivity to epoxide compared to the 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%.

KEY WORDS: carbon–silica composite; epoxidation; hydrogen peroxide; activated carbon; titanium-containing catalysts.

1. Introduction

The development of new titanium-containing catalysts and their modification is of great importance in the field of liquid-phase oxidation reactions using heterogeneous catalysts. The first effort of incorporating titanium into zeolite was carried out by researchers of Enichem that led to the TS-1 catalyst. This then indeed opened a new area of selective epoxidation of linear olefins and oxidation reactions of alcohols, alkanes, aromatics, etc. [1–5]. Since the discovery of TS-1, various titanium-containing catalysts have been synthesized, such as Ti-beta, TiO_2–SiO_2 mixed oxides and Ti-mesoporous materials, which are silica-based catalysts [6–8]. However, these catalysts have a serious shortcoming in their catalytic activity for the epoxidation of olefins because of their hydrophilic surface character. The hydrophilic character induces side reactions of epoxidation and thus considerably decreases the efficiency of the catalysts in the above mentioned catalytic reactions.

In recent years, the silylation technique for the modification of mesoporous molecular sieves has received much attention as one way to overcome such a drawback. Several authors reported that some silylating agents, such as trimethylsilyl chloride (TMSCl), hexamethyldisiloxane (HMDS), bis(trimethylsilyl) trifluoroacetamide (BSTFA), *N*-trimethylsilyl imidazole (TMSI) and *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA), were effective to silylate Ti-MCM-41 or Ti-MCM-48 [9–14] and to increase both the hydrophobicity and the epoxidation activity. 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 solvents under certain conditions [15,16].

Activated carbon materials have been used in heterogeneous catalysis for a long time because they can either be used directly as catalysts or satisfy most of the desirable properties required for suitable supports [17]. Activated carbon has useful properties such as stability and unique surface properties. In particular, carbon has a hydrophobic surface property and contains various functional groups in substantial amounts. These surface properties can be utilized for the synthesis of titanium-containing catalysts and suppress side reactions of epoxidation compared to titanium silicate catalysts.

In this work, we synthesized titanium-containing activated carbon and silica–carbon composite catalysts and examined whether these catalysts may give rise to a better epoxide selectivity in the liquid-phase epoxidation of cyclohexene. For this purpose, the catalysts were prepared by a surface coating method using tetraethyl orthosilicate (TEOS) as the silica source and also by a surface grafting method. They were applied to the epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP) and H_2O_2. We further synthesized titanium-grafted amorphous silica and Ti-MCM-41 to compare the catalytic performance with the titanium-loaded carbon–silica composite catalysts.

2. Experimental

2.1. Preparation of the 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.

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The carbon–silica composite was prepared by the following method. The activated carbon was dried and TEOS/ethanol (anhydrous) solution was then introduced to the activated carbon. The synthesis of the 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 the 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 thoroughly washed 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 $Ti(O^iPr)_4$ (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 $Ti(O^iPr)_4$ and subsequently dried at 383 K for 24 h. Since the carbon support could be burned off in the presence of oxygen, carbon catalysts were only dried. For the purpose of comparison, Ti-MCM-41 was synthesized using the procedure reported elsewhere [18] 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.

2.2. *Characterization of the catalysts*

The concentration of functional groups on the carbon surface was determined by Boehm's titration method [19]. The contents of silica and titanium of the carbon-supported catalysts were measured by ICP using a Shimadzu ICPQ 1000 spectrometer. The Ti-MCM-41 and titanium-grafted silica were identified by FTIR and UV–vis spectroscopy [20–23].

Table 1
Titanium-containing catalysts prepared in this work

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

2.3. *Epoxidation of cyclohexene*

In a typical procedure, 100 mg of catalyst and 20 mmol of cyclohexene were 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 a gas chromatograph equipped with an HP-5 capillary column and FID detector using cyclohexane as the internal standard. The products were confirmed by comparison with authentic samples and GC–MS analysis.

3. Results and discussion

3.1. *Preparation of the catalysts*

The surface nature of the activated carbon was analyzed by Boehm's titration method and the surface area of the catalyst support was measured by BET analysis. Table 2 gives the results. According to

Table 2
Physicochemical properties of activated carbon and catalysts prepared

Boehm's titration analysis			
Activated carbon	Amount of 0.05 N HCl consumed in back-titration (ml)		
	NaOH	Na_2CO_3	$NaHCO_3$
	15.0	17.0	18.6
	Amount of functional groups (mmol/g)		
	Hydroxyl group	Lactone	Carboxyl acid
	0.25	0.20	0.18

BET analysis								
Catalyst	Ti–silica	Ti-MCM-41	Activated carbon	Ti–carbon	Ti–carbon silica A	Ti–carbon silica B	Ti–carbon silica C	Ti–carbon silica D
Surface area (m^2/g)	540	987	1490	1254	935	780	652	532

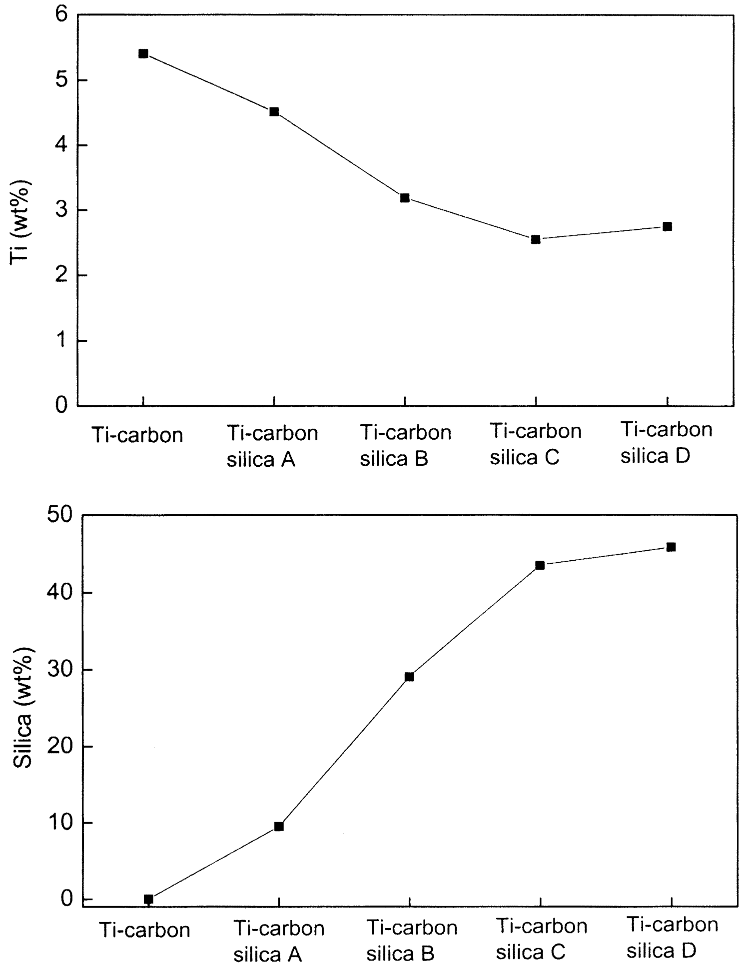

Figure 1. Contents of titanium and silica in the catalysts.

these results, the activated carbon has a large surface area and contains ~0.25 mmol/g of hydroxyl group, ~0.20 mmol/g of lactone and ~0.18 mmol/g of carboxyl acid. The activated carbon has good surface properties as a support for catalysts for grafting reactions because it has a large surface area and a high content of functional groups. In the case of carbon–silica composites, the surface area tends to decrease as the silica content increases. These materials, however, still have sufficient surface areas for use as catalyst supports.

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 ~0.63 mmol/g. If all the functional groups react with $Ti(O^iPr)_4$, the activated carbon would contain almost 3 wt% titanium. Since the titanium grafting reaction was performed under anhydrous conditions, the hydrolysis of $Ti(O^iPr)_4$ 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 a silica support [21–23].

The activated carbon contains various functional groups. Each of these functional groups shows a different activity in the alkoxide grafting reaction. The most active functional group reacts first with $Ti(O^iPr)_4$. After this step, the $Ti(O^iPr)_4$ could be attached to different sites. One is the residual functional group and the others are titanium species previously attached to the carbon surface and unreacted $Ti(O^iPr)_4$. The large amount of grafted titanium may be attributed to these reaction phenomena. A similar result was observed when the grafting of $Ti(O^iPr)_4$ was carried out on a silica support [21–23]. This catalyst is denoted by Ti–silica in table 1.

The carbon–silica composite was prepared by silica coating on the carbon surface. As the concentration of silicon alkoxide increased, the content of silica on carbon was increased. This result was due to the surface coating method, which is different from the titanium post-synthesis method. This surface treatment induced the hydrolysis of TEOS and the polymerization of silica precursor on the carbon surface. In the initial reaction step, the TEOS molecules were mainly attached to the carbon surface by a condensation reaction, then the TEOS was slowly hydrolyzed by the addition of a small amount of H_2O and the hydrolyzed TEOS was polymerized with silica on the carbon surface. In the final reaction step, the silica network covered the

Table 3
Results of cyclohexene epoxidation using TBHP and H_2O_2 as the oxidants

Catalyst	Oxidant	Yield of epoxide (%)	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

carbon surface. This means that the silica coating method can increase the silica content to a higher level than the grafting method.

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 the activated carbon, the surface area of the 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 decreased with the silica loading.

3.2. Cyclohexene epoxidation over various catalysts

Table 3 shows the yield of cyclohexene and the selectivity to each of the products over the various catalysts when TBHP or H_2O_2 was used as the oxidant. Both the silica-based catalysts, Ti–silica and Ti-MCM-41, show a good catalytic activity with TBHP as the oxidant, whereas the selectivity to epoxide decreases drastically when H_2O_2 is used as the oxidant. This phenomenon may be explained in terms of the hydrophilic surface properties caused by the surface silanol groups. Water and hydrogen peroxide are strongly adsorbed on these catalysts, yielding a very low cyclohexene concentration on the catalyst surface, and thus the catalytic performance reduced [24].

However, this is not the case with the Ti–carbon catalyst. The hydrophobic surface property of the activated carbon promotes attack on the C=C bond in cyclohexene to produce more epoxide. Since the presence of water on the surface is responsible for the ring opening of the epoxide to form a diol, the relative amount of diol decreases almost linearly with the increase of hydrophobicity [9]. On the other hand, the hydrophobic nature of the carbon surface suppresses the formation of 1-ol and 1-one. However, the selectivities to diol, 1-ol and 1-one are still high compared with those of carbon–silica composite catalysts when the reaction was carried out with H_2O_2 as oxidant. It seems that the Ti–carbon catalyst contained some of the residual functional groups and polymeric species of titanium. These species must have promoted the formation of diol, 1-ol and 1-one. Although the Ti–carbon catalyst has a higher selectivity to epoxide than the silica-based catalysts, the conversion of cyclohexene is still low compared with that over the silica-based catalysts.

According to Oldroyd *et al.* [25] a significant effect was observed on the catalytic activity in the epoxidation of cyclohexene when the surface of silica was modified with either Ge(IV) or Sn(IV) prior to the grafting of Ti(IV). Similarly, the local environment of Ti on the activated carbon would be different from that of Ti on the silica surface and the catalytic activity of Ti on the silica is better than that of Ti on the activated carbon. Hence, silica was introduced on the activated carbon surface to reduce the amount of residual functional groups and enhance the catalytic activity.

The reaction results presented in table 3 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. Moreover, when H_2O_2 was used as the oxidant, the composite-based catalysts show a much better epoxide selectivity than the Ti–carbon catalyst and the yield of epoxide increased to almost twice that over the silica-based catalysts.

The amount of titanium loaded on the support shows a different reaction trend. The reaction results show that the diol selectivity increased with the titanium content in the carbon–silica composites. The Ti–carbon silica B catalyst, which contained about 3 wt% of titanium, shows the highest yield of epoxide. Yun *et al.* [26] reported that both the activity and the selectivity to epoxide were increased with Ti content up to ~3 wt%. When the titanium content was larger than ~3 wt%, the extra-framework titanium gave rise to a lower activity as well as a lower selectivity to epoxide. The extra titanium can block the active site and act as an acid site so that it can promote the formation of by-products.

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 centers on the silica support.

4. Conclusions

The carbon–silica composite material was found to be a good support for the titanium-containing catalysts. Titanium could be loaded successfully on the carbon–silica composite by the post-synthesis method. When applied to the epoxidation of cyclohexene, the Ti-containing carbon–silica composite showed an increased selectivity to epoxide with TBHP used as the oxidant. When H_2O_2 was employed as the oxidant, the catalytic performance of these catalysts was substantially improved for both the epoxide yield and the selectivity to epoxide. This may be attributed to the hydrophobic nature of the carbon surface and the local environment of active Ti centers on the silica support. The best performance was obtained with the carbon–silica composite containing about 3 wt% of Ti, which is consistent with a previous report.

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