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Article

Preparation and catalytic property of modified multi-walled carbon nanotube-supported TiO_2 for the transesterification of dimethyl carbonate with phenol

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ARTICLE INFO

Article history:

Received 7 November 2013

Accepted 24 December 2013

Published 20 April 2014

Keywords:

Multi-walled carbon nanotube

Titanium dioxide

Diphenyl carbonate

Transesterification

Precipitant

ABSTRACT

Modified multi-walled carbon nanotube-supported TiO_2 samples were prepared and used as an efficient heterogeneous catalyst for the transesterification of dimethyl carbonate with phenol. The catalysts were characterized by X-ray photoelectron spectroscopy, transmission electron microscopy, N_2 adsorption-desorption, and X-ray powder diffraction. The results showed that the catalyst, which was prepared using a low concentration (0.4%) of ammonium hydroxide as the precipitant instead of ionized water, had better catalytic activity, separability, and reusability properties. The effects of the TiO_2 loading, amount of catalyst and reaction time on the performance of the transesterification reaction were also studied. Under the optimum reaction conditions, the conversion of phenol reached 42.5% with over 99.9% selectivity for methyl phenyl carbonate and diphenyl carbonate. The catalyst could be reused for the transesterification in four runs with only slight loss of its catalytic activity.

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1. Introduction

Diphenyl carbonate (DPC) is used to produce many fine chemicals and polymer materials, especially where it is used as an intermediate for the phosgene-free synthesis of polycarbonate. Several processes have been developed for the synthesis of DPC, including the phosgene process [1], the oxidative carbonylation of phenol [2–4], and the transesterification of phenol with dimethyl oxalate [5] or dimethyl carbonate (DMC) [6]. The transesterification of DMC with phenol is the most environmentally attractive of these processes for commercial production of DPC [7].

A wide range of efficient homogeneous catalysts have been

reported for the transesterification of DMC with phenol, including organic Sn, Ti, Fe and Sm complexes [8–11]. The use of homogeneous catalysts for this transformation, however, has been limited because of problems associated with their separation from the product, and research towards the development of heterogeneous catalysts for this reaction has consequently attracted considerable attention. Several heterogeneous catalysts have been reported for this reaction, including transition metal oxides [12–23], such as TiO_2 , MoO_3 , V_2O_5 , V-Cu mixed oxide, PbO , $\text{TiO}_2/\text{SiO}_2$, and $\text{MoO}_3/\text{SiO}_2$. Although some of these catalysts performed with suitable activity, their selectivity and reusability properties were not satisfactory. For this reason, there is an urgent need for the development of a highly efficient

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This work was supported by the National High Technology Research and Development Program of China (863 Program, SS2013AA031703) and Sichuan Provincial Scientific Innovation Team of China (2013TD0010).

DOI: 10.1016/S1872-2067(14)60010-3 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 4, April 2014

heterogeneous catalyst for the synthesis of DPC.

Carbon nanotubes (CNTs) represent a promising catalyst support because of their unique and outstanding mechanical, electronic, and chemical properties. CNT-supported catalysts have been used in a wide range of chemical transformations, including hydrogenation reactions, Fischer-Tropsch synthesis, hydroxylation of benzene, and photo-catalysis [24–26]. We recently reported the preparation of TiO_2 supported on unmodified multi-walled carbon nanotubes ($\text{TiO}_2/\text{MWCNTs}$) in the presence of a surfactant and its use as a catalyst for the transesterification of DMC with phenol [27]. The results showed that the $\text{TiO}_2/\text{MWCNTs}$ exhibited excellent activity and selectivity. Unfortunately, its reusability was poor, with the separation of the catalyst from product by centrifugation being particularly time consuming. Furthermore, traces of surfactant were found in the reaction system, which made the purification of the product very difficult.

Herein, we develop a method for the preparation of a readily separable, efficient and reusable heterogeneous catalyst by the controlled hydrolysis of a Ti precursor to form TiO_2 following deposition on the surface of an oxidative modified MWCNT ($\text{TiO}_2/\text{o-MWCNT}$). Our results revealed that the species and concentration of the precipitants had a remarkable effect on the activity, stability and separability of the $\text{TiO}_2/\text{o-MWCNTs}$ for the transesterification of DMC with phenol.

2. Experimental

2.1. Materials and reagents

DMC was obtained from Huasheng Co. Ltd., Shangdong University of Petroleum, China. Phenol (AR), ethanol (AR), and ammonia water (25–28%, AR) were purchased from Guangdong Guanghua Sci-Tech Co. Ltd., China. The MWCNTs (inner diameter: 4–8 nm, outer diameter: 10–30 nm) were obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, China. All of the materials and reagents were used directly without further purification.

2.2. Preparation of $\text{TiO}_2/\text{MWCNT}$

The MWCNTs were initially treated with an acidic KMnO_4 solution to remove any impurities and improve its solubility. Briefly, the MWCNTs (20 g) and solid KMnO_4 (60 g) were added to sulfuric acid (6 mol/L, 800 ml), and the resulting mixture was stirred at 100 °C for 1.5 h. The suspension was then cooled to room temperature and filtered, and the solid was collected and suspended in concentrated HCl to remove any of the MnO_2 formed during the process. The suspension was then filtered and the filter-cake was washed with deionized water until neutral before being dried in an oven at 120 °C for 8 h.

Typical procedure for the preparation of the $\text{TiO}_2/\text{o-MWCNTs}$: The o-MWCNTs (1.2 g) and ammonium hydroxide (25%–28%, 0.6–10 ml) were dispersed in ethanol (180 ml) with ultrasonic treatment for 1 h. Tetrabutyl titanate (0.5–1.5 ml) was dispersed in ethanol (20 ml) and added to the o-MWCNT suspension in a drop-wise manner under vigorous

stirring. The resulting mixture was stirred at 45 °C for 12 h to complete the hydrolysis reaction before being cooled to ambient temperature and filtered. The filter-cake was then washed sequentially with deionized water and ethanol (3 times) before being collected and dried in an oven at 120 °C for 4 h. The dried material was calcined at 200 °C for 3 h in air to obtain the powdered $\text{TiO}_2/\text{o-MWCNTs}$.

The TC-A-0.3, TC-A-0.4, TC-A-0.5, TC-A-0.6, and TC-A-7.5 samples represent the $\text{TiO}_2/\text{o-MWCNTs}$ prepared using 0.3%, 0.4%, 0.5%, 0.6%, and 7.5% (based on ethanol) ammonium hydroxide (25%–28%) as the precipitant, respectively. The TC-W-0.4, TC-W-0.5, TC-W-0.6, and TC-W-7.5 samples represent the $\text{TiO}_2/\text{o-MWCNTs}$ prepared using 0.4%, 0.5%, 0.6%, and 7.5% (based on ethanol) deionized water as the precipitant, respectively.

2.3. Characterization of $\text{TiO}_2/\text{MWCNT}$

X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (Philip XPERT PRO MPD) using a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.154056 \text{ nm}$), operating at 40 kV and 45 mA. The system was operated in the continuous mode to allow for the collection of data at a scanning speed of $0.02^\circ/\text{s}$. The surface electronic structures of the catalysts were detected by X-ray photoelectron spectroscopy (XPS) on a Kratos Model XSAM 800 instrument using a monochromatic and focused (350W) $\text{Mg K}\alpha$ (1253.6 eV) radiation source. Transmission electron microscopy (TEM) studies were conducted on a JEM-1000CX TEM system operating at an accelerating voltage of 80 kV. The specific surface area (A_{BET}), pore size (BJH), and pore volume of the catalysts were calculated from low temperature N_2 adsorption-desorption isotherms using a TriStar II 3020 system (Micromeritics Instrument Corporation). The Ti content of the filtrate was determined using a TS IRIS 1000 ICP-AES instrument.

2.4. Transesterification of DMC with phenol

The transesterification reaction was carried out in a 100 ml three-neck round-bottomed flask equipped with a magnetic stirring bar, a nitrogen inlet, a dropping funnel, and a fractionating column connected to a liquid dividing head. Phenol and the catalyst were added to the flask under N_2 atmosphere, and the resulting mixture was heated in the range of 175–178 °C. DMC was then added to the mixture in a drop-wise manner under continuous stirring. During the reaction, a distillate composed of DMC and methanol was collected in a receiver flask attached to the liquid dividing head. Upon completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated by centrifugation. The filtrate and distillate were quantitative analyzed by GC system (Agilent Technologies 7820A) equipped with an FID detector and a DB-35 capillary column (30 m $\times$ 320 μm $\times$ 0.25 μm). The GC results were calculated using a correction factor normalization method. The structure of the product was defined by GC-MS on a HP 6890/5973 system. In the experiment designed to test the reusability of catalyst, the catalyst was separated by filtration

and washed with DMC before being dried in an oven and then reused in the next reaction.

3. Results and discussion

3.1. Characterization results of catalysts

3.1.1. XPS analysis

TC-W-0.5 and TC-A-0.4 were analyzed by XPS to investigate the atomic composition and corresponding chemical states on the surfaces of these TiO₂/o-MWCNT catalysts. The atomic surface compositions are shown in Table 1. The results revealed that the amount of surface Ti on the TC-A-0.4 catalyst was slightly higher than that of TC-W-0.5. The ICP-AES analysis, however, revealed that the TiO₂ loading of TC-A-0.4 was much lower than that of TC-W-0.5 (Table 2). These results indicated that the dispersion of TiO₂ on the surface of the o-MWCNTs was enhanced by the use of ammonia hydroxide as the precipitant instead of deionized water. Furthermore, there were about 1.28% N atoms on the surface of the TC-A-0.4 catalyst. The N atoms belonged to the amide that was formed by the reaction of ammonia with the carboxyl groups on the surface of the o-MWCNTs.

As shown in Fig. 1(a), the electron binding energy of Ti 2p_{3/2} and Ti 2p_{1/2} for TC-A-0.4 was 459.2 and 464.9 eV, respectively, representing a shift of 0.4 eV towards a higher binding energy compared with pure bulk anatase. This result indicated that the Ti on the surface of the TiO₂/o-MWCNTs was in a different environment to that of pure anatase. As shown in Fig. 1(b), the electron binding energy of Ti 2p_{3/2} and Ti 2p_{1/2} for TC-W-0.5 was 458.9 and 464.6 eV, respectively, representing a shift of 0.3 eV towards a lower binding energy compared with TC-A-0.4. Taken together, these results suggested that the Ti in the TC-A-0.4 and TC-W-0.5 catalysts were not in the same chemical

Table 1

Atomic surface compositions of the catalyst detected by XPS.

Sample	Surface composition (%)			
	C	O	N	Ti
TC-W-0.5	79.36	17.58	0	3.06
TC-A-0.4	79.92	15.66	1.28	3.14

Table 2

Physicochemical properties of the catalysts.

Sample	TiO ₂ loading (%)	A _{BET} (m ² /g)	Average pore size (nm)	Total pore volume (cm ³ /g)
o-MWCNT	0	136	3.8	0.1935
TC-W-0.5	17.5	152	3.6	0.1910
TC-A-0.4	10.8	161	3.6	0.1948
TC-A-7.5	25.8	186	3.1	0.1956

environment.

Figure 1(c) and 1(d) show the C 1s spectra of TC-A-0.4 and TC-W-0.5, respectively. Each C 1s spectra could be deconvoluted into four peaks. For TC-A-0.4, the peaks at 284.6, 285.8, 287.2, and 289.1 eV were attributed to the C–C, C–O, C=O, and O–C=O bonds, respectively. The presence of these oxygen containing functional groups confirmed that the surfaces of the MWCNTs had been successfully modified by the oxidation, which provided anchors for the immobilization of the TiO₂. The O 1s spectra of TC-A-0.4 and TC-W-0.5 are shown in Fig. 1(e) and (f), respectively. Each O 1s spectra could be deconvoluted into three peaks. For TC-A-0.4, the peaks at 531.1, 532.6, and 534.0 eV were attributed to the Ti–O, C–O, and C=O bonds, respectively. As shown in Fig. 1(g), the N 1s spectrum of TC-A-0.4 consisted of two peaks at 400.1 and 402.1 eV, which were attributed to pyrrole-like nitrogen and C–N of the amide group, respectively.

3.1.2. TEM analysis

Fig. 1. XPS spectra of the TiO₂/o-MWCNTs: (a) Ti 2p spectra of TC-A-0.4; (b) Ti 2p spectra of TC-W-0.5; (c) C 1s spectra of TC-A-0.4; (d) C 1s spectra of TC-W-0.5; (e) O 1s spectra of TC-A-0.4; (f) O 1s spectra of TC-W-0.5; (g) N 1s spectra of TC-A-0.4.

Fig. 2. TEM images of TC-A-0.4 (a), TC-W-0.5 (b), TC-A-7.5 (c), and TC-W-7.5 (d) catalysts.

The TEM images of the different catalysts are shown in Fig. 2. It showed that the TiO_2 particles were uniformly dispersed on the surfaces of TC-A-0.4 without any agglomeration [Fig. 2(a)]. The concentration of TiO_2 particles on the tip of the o-MWCNTs was slightly higher than that on the sidewall of the o-MWCNTs, which was attributed to the higher density of oxygen containing functional groups on the tip of o-MWCNTs. This was in agreement with the reported results [24–26]. As shown in Fig. 2(b), some of the TiO_2 particles agglomerated on the surface of the o-MWCNTs, indicating that the dispersion of TC-W-0.5 (0.5% deionized water as the precipitant) was less effective than that of TC-A-0.4 (0.4% ammonium hydroxide as the precipitant). These results were in agreement with the XPS result. When the concentration of precipitant was increased to 7.5%, the agglomeration of the TiO_2 particles increased significantly on the surfaces of the o-MWCNTs, regardless of whether ammonium hydroxide (Fig. 2(c)) or deionized water (Fig. 2(d)) was used as the precipitant.

3.1.3. N_2 adsorption-desorption

The BET surface area, pore size, and pore volume of the catalysts were summarized in Table 2. The results revealed that the specific surface area increased, whereas the average pore size decreased following the supporting of the TiO_2 particles for all catalysts. According to the TEM and XRD results, the active TiO_2 components were well dispersed on the surfaces of the o-MWCNTs in an amorphous state. The A_{BET} of the porous TiO_2 was larger than that of the o-MWCNTs, which resulted in the higher A_{BET} of the $\text{TiO}_2/\text{o-MWCNTs}$. These results were consistent with those previously reported in the literature [24–27]. Although more TiO_2 particles had been supported on the surface of TC-W-0.5, the BET surface area of TC-A-0.4 was higher than that of TC-W-0.5. These results indicated that the TiO_2 particles were distributed more uniformly on the surface of TC-A-0.4, which was in good agreement with the XPS and TEM results. There are two possible reasons for the decrease in the average pore size of the $\text{TiO}_2/\text{o-MWCNTs}$ compared with the o-MWCNTs, including (1) the pore size of the TiO_2 was smaller than that of the o-MWCNTs, and (2) partial TiO_2 particles were introduced into the channels of the o-MWCNTs, resulting in a

decrease in the diameter of o-MWCNTs. Furthermore, there were no discernible changes in the pore volumes of TC-W-0.5, TC-A-0.4, and TC-A-7.5 compared with the o-MWCNTs.

3.1.4. XRD analysis

Figure 3 shows the XRD patterns of the o-MWCNTs and $\text{TiO}_2/\text{o-MWCNTs}$ samples. All samples showed three obvious diffraction peaks at 25.8° , 42.7° , and 53.3° , corresponding to the (002), (100), and (004) diffractions of the hexagonal graphite in the o-MWCNTs, respectively. The peak intensity of the $\text{TiO}_2/\text{o-MWCNTs}$ was lower than that of the o-MWCNTs, because the partial surface of the o-MWCNTs was covered with TiO_2 . As expected, the characteristic diffraction peaks of the TiO_2 crystals were not found in the TC-A-0.4, and TC-A-7.5 samples prepared by calcinating at 200°C , because the calcination temperature was too low to transform the amorphous TiO_2 into its crystal form. There were four diffraction peaks at 25.4° , 37.8° , 47.9° and 62.7° corresponding to the (101), (004), (200), and (204) of anatase TiO_2 over TC-A-7.5 calcinated at 400°C , respectively. However, the characteristic diffraction peaks of crystalline TiO_2 were not found in the TC-A-0.4 calcinated at 400°C . The difference could be due to that the TiO_2 was well dispersed on the surface of the o-MWCNTs when a low concentration of the precipitant was used.

3.2. Catalytic activity for the transesterification of DMC with phenol

There are two steps involved in the synthesis of DPC from DMC and phenol, including the transesterification of DMC with phenol to form methyl phenol carbonate (MPC) (reaction 1), and the further transesterification of MPC with phenol (reaction 2) or the disproportionation of MPC (reaction 3, main process) to obtain DPC. The formation of MPC is the key step because the thermodynamic equilibrium constants for reactions 1, 2, and 3 are 6.3×10^{-5} , 1.2×10^{-5} , and 0.19, respectively. The properties of a catalyst for this transformation are usually evaluated by the total selectivity and yield of MPC and DPC. Furthermore, the total reaction of DMC with phenol is an equi-

Fig. 3. XRD patterns of the o-MWCNTs and $\text{TiO}_2/\text{o-MWCNTs}$ catalysts. (1) o-MWCNTs; (2) TC-A-0.4 calcined at 200°C ; (3) TC-A-7.5 calcined at 200°C ; (4) TC-A-0.4 calcined at 400°C ; (5) TC-A-7.5 calcined at 400°C .

librium reaction. The methanol byproduct can be removed by azeotropic distillation with DMC to promote the reaction towards the formation of MPC and DPC. The amount of DMC used in the transformation is therefore usually greater than that of the theoretically required dosage. Based on our previous work [7,9–11,27], the optimum molar ratio of DMC to phenol was 1:1.

For comparison, the o-MWCNTs and TiO₂ were initially used directly as the catalyst for the transesterification of DMC with phenol. As shown in Table 3, MPC and DPC were not detected in the reaction mixture when the o-MWCNT was used. Although TiO₂ promoted the reaction, its activity was relatively low [28]. The catalytic properties of the TiO₂/o-MWCNTs prepared under the same conditions, except for the concentration and/or type of precipitant, were also investigated, and the results are summarized in Table 3. As previously reported in the literatures [8–21], this reaction would lead to the formation of anisole. The yield of anisole, however, was less than 0.03% for all of the catalytic reactions evaluated in the current study, which resulted in the very high total selectivity of MPC and DPC. The activity of the TiO₂/o-MWCNTs could be varied by changing the concentration and/or type of precipitant during the preparation process. When deionized water was used as the precipitant, the conversion of phenol initially increased from 33.7% to 39.0% as the concentration of water was increased from 0.4% to 0.5%. The conversion of phenol decreased slightly to 36.9% when the concentration of water was further increased to 0.6%. When the concentration of water was increased to 7.5%, the phenol conversion decreased significantly to 28.2%. A similar result was obtained for the catalysts prepared using ammonium hydroxide. When the amount of ammonium hydroxide was raised from 0.3% to 0.6%, the conversion of phenol also increased initially and then decreased, with the highest phenol conversion being 39.5%. A phenol conversion of only 20.4% was observed when the amount of ammonium hydroxide was increased to 7.5%. Two possible explanations were provided for these results: (1) the loading of the TiO₂ increased as the concentration of the precipitant increased; (2) the agglomeration of the TiO₂ particles would increase as the concentration of precipitant increased. It is noteworthy that most of the TiO₂/o-MWCNT catalysts

Fig. 4. Photographs showing the separation of catalyst from the product mixture. (a) TC-W-0.4; (b) TC-W-0.5; (c) TC-A-0.4; (d) TC-A-0.5.

showed higher activity than TiO₂, which could be attributed to the interaction between the active TiO₂ component and the o-MWCNT support. These results were in agreement with those previously published in the literatures [20,27].

As expected, the calcination temperature had a remarkable effect on the activity of the TiO₂/o-MWCNTs towards the transesterification of DMC with phenol. The conversion of phenol decreased quickly from 39.5% to 12.2% as the calcination temperature was increased from 200 to 400 °C. The reason for this decrease was that the morphology of TiO₂ changed from the amorphous to the anatase state at 400 °C, and this process was confirmed in our previous study [27]. Although the characteristic peak of anatase TiO₂ was not found in the TC-A-0.4 calcined at 400 °C, it was clearly present in the TC-A-7.5 calcined at 400 °C (Fig. 3). The characterization results also indicated that the TiO₂ was well dispersed on the surfaces of the MWCNTs constructed with a low concentration of ammonium hydroxide.

In addition, we found that TC-W-0.4 and TC-W-0.5 prepared using water as the precipitant were difficult to separate from the mixture upon completion of the reaction. As shown in Fig. 4 (a) and (b), these catalysts could not be completely separated even under centrifugation at a speed of 4000 r/min for 2 h. Although they could be separated by high-speed centrifugation (10000 r/min), their application was limited by the requirement for such harsh separation conditions. In contrast, the TC-W-7.5 catalyst could be readily separated from the reaction

Table 3

Catalytic properties of the TiO₂/o-MWCNTs.

Catalyst	Precipitant concentration (%)	TiO ₂ loading (%)		Phenol conversion (%)	Yield (%)		Separability
		Calculated	Detected		MPC	DPC	
o-MWCNT	—	—	—	—	—	—	Difficult
TiO ₂	—	—	—	18.7	12.0	6.7	Easy
TC-W-0.4	H ₂ O (0.4)	26.7	13.8	33.7	14.4	19.3	Difficult
TC-W-0.5	H ₂ O (0.5)	26.7	17.5	39.0	18.5	20.5	Difficult
TC-W-0.6	H ₂ O (0.6)	26.7	20.5	36.9	17.9	19.0	Difficult
TC-W-7.5	H ₂ O (7.5)	26.7	26.0	28.2	14.5	13.7	Moderate
TC-A-0.3	NH ₄ OH (0.3)	26.7	8.3	38.4	17.9	20.5	Easy
TC-A-0.4	NH ₄ OH (0.4)	26.7	10.8	39.5	17.9	21.6	Easy
TC-A-0.5	NH ₄ OH (0.5)	26.7	14.2	36.4	16.6	19.8	Easy
TC-A-0.6	NH ₄ OH (0.6)	26.7	21.7	34.8	18.4	16.4	Easy
TC-A-7.5	NH ₄ OH (7.5)	26.7	25.8	20.4	11.9	8.5	Easy
TC-A-0.4 calcined at 400 °C	NH ₄ OH (0.4)	26.7	10.8	12.2	9.5	2.7	Easy

Reaction conditions: DMC 0.16 mol, phenol 0.16 mol, catalyst 0.4 g, 180 °C, 9 h.

mixture under centrifugation at a speed of 4000 r/min for 15 min. Furthermore, the catalysts prepared using ammonium hydroxide instead of water as a precipitant were readily separated from the reaction mixture, and centrifugation was not necessary in these cases because the catalysts were automatically deposited within 3–5 min, as shown in Fig. 4(c) and (d).

It is well known that oxidatively modified CNTs can be well dispersed in polar solvents because of the hydrophilic nature of the oxygen containing functional groups on their surface. The reason for the difficulties encountered during the separation of the TC-W-0.4 and TC-W-0.5 catalysts could be that large numbers of oxygen containing functional groups were still exposed on the surfaces of catalysts. Certainly, the number of oxygen containing functional groups on the surfaces of the CNTs reduced with increasing TiO_2 loading, which resulted in the catalysts being more readily separated (e.g., TC-W-7.5). When ammonium hydroxide was used as the precipitant instead of water to prepare the catalysts, the nucleation and growth of the metal oxides occurred prior to the formation of the oxygen containing functional groups of the CNTs, as reported in the literature [24–26]. The corresponding catalysts (TC-A-0.4 and TC-A-0.5) exhibited hydrophobic behavior since most of their oxygen containing functional groups had been covered by hydrophobic TiO_2 , which resulted in the catalyst being easy to separate from the product.

3.3. Effect of TiO_2 loading on the transesterification

$\text{TiO}_2/\text{o-MWCNT}$ catalysts with different TiO_2 loadings were prepared by using 0.4% ammonium hydroxide as the precipitant, in a manner similar to that of the preparation of TC-A-0.4. The effect of the TiO_2 loading on the transesterification of DMC with phenol was investigated, and the results are shown in Fig. 5. The conversion of phenol increased from 35.0% to 39.5% as the TiO_2 loading (actual loading, detected by ICP-AES) was increased from 4.5% to 10.8%. The conversion of phenol, however, decreased slightly when the TiO_2 loading was increased further to 20.1%. The reason for this reduction in the conversion could be that the excess TiO_2 loading would lead to the aggregation of TiO_2 on the surface of the o-MWCNTs. Further-

Fig. 5. Effect of the TiO_2 loading on the transesterification of DMC with phenol. Reaction conditions: DMC 0.16 mol, phenol 0.16 mol, the catalyst 0.4 g, 180 °C, 9 h.

more, the total yield of MPC and DPC exhibited a similar trend to the conversion of phenol, and the selectivity of the byproduct (anisole) was lower than 0.03% for all of the catalytic reactions.

3.4. Effect of catalyst amount on the transesterification

The effect of TC-A-0.4 amount on the transesterification was also investigated. As shown in Fig. 6, the conversion of phenol increased from 31.1% to 42.5% as the catalyst amount was increased from 0.68% to 2.04% (based on the total raw material). Further increasing the catalyst amount to 2.72% led a slight increase in the phenol conversion to 44.2%. When the catalyst amount was further increased to 3.40%, no discernible difference was observed in the conversion of the phenol. Because the o-MWCNT catalytic support possessed good adsorption capability and low density, it was envisaged that an expansion phenomenon would be observed in the reaction system when a large amount of catalyst was used. The expansion of reaction mixture would lead to problems in terms of mass transfer and separation. Following comprehensive consideration, the optimum amount of catalyst was set at 2.04%.

3.5. Effect of reaction time on the transesterification

The effect of the reaction time on the yield of MPC and DPC was also investigated because the transesterification of DMC with phenol is a reversible reaction. As shown in Fig. 7, the conversion of phenol increased as the reaction time was increased from 7 to 13 h using TC-A-0.4 as catalyst, with the highest phenol conversion reached being 49.2%. The phenol conversion effectively reached a plateau at this point, with further increases in the reaction time providing a similar conversion. According to the results of thermodynamic analyses reported previously in the literature [21,29], the conversion observed in our study was close to the theoretical equilibrium value. The yield of DPC increased continuously with increasing reaction time. The yield of MPC, however, initially increased as the reaction time was increased from 7 to 9 h, and then decreased as the reaction time was increased further to 15 h. This could be attributed to the rate of MPC formation being lower

Fig. 6. Effect of TC-A-0.4 amount on the transesterification of DMC with phenol. Reaction conditions: DMC 0.16 mol, phenol 0.16 mol, 180 °C, 9 h.

Fig. 7. Effect of the reaction time on the transesterification of DMC with phenol. Reaction conditions: DMC 0.16 mol, phenol 0.16 mol, using TC-A-0.4 of 0.6 g (2.04% based on total material), 180 °C.

than that of MPC to DPC after 9 h. Given that most of the unreacted DMC would have been removed from the reaction system through azeotropic distillation with methanol after 9 h, the rate of MPC formation would be very low. During this period, the main reaction process would be the disproportionation of MPC to DPC, which would result in a decrease in the MPC yield and an increase in the DPC yield. Furthermore, the total selectivity was always higher than 99% even after an extended reaction time of 15 h.

3.6. Reusability test

It has been reported that the active component can be lost from the catalyst during the transesterification of DMC with phenol [20]. Owing to the strong interaction between TiO_2 and the CNTs, the leaching of TiO_2 could be greatly reduced from the surface of the CNTs [27]. With this in mind, we evaluated the reusability of TC-W-0.5 and TC-A-0.4 catalysts. Upon completion of the reaction, the catalyst was filtered, washed with DMC, dried under vacuum, and reused for the next run. As shown in Table 4, leaching of TiO_2 still occurred from the TC-W-0.5 and TC-A-0.4 catalysts. The level of TiO_2 leaching from TC-W-0.5, however, was much greater than that from TC-A-0.4. In the first run, the level of TiO_2 leaching from

TC-W-0.5 was up to 27%. Furthermore, the total TiO_2 leaching from TC-W-0.5 reached about 51% after three runs, and was accompanied by a reduction in the conversion of phenol to only 19.2%. In comparison, TiO_2 leaching from TC-A-0.4 was only 12% after the first run. Furthermore, the total TiO_2 leaching from TC-A-0.4 was about 20% after three runs, resulting in a reduction in the conversion of phenol from 39.5% to 33.5%. These differences could be attributed to differences in the dispersions of TC-W-0.5 and TC-A-0.4. As shown in the TEM and XPS results, the agglomeration of TiO_2 particles was observed on the surfaces of the o-MWCNTs for TC-W-0.5, whereas the TiO_2 particles were well dispersed for TC-A-0.4. It was envisaged that the interaction between TiO_2 and the o-MWCNTs would decrease as the thickness of the TiO_2 particles increased. The level of TiO_2 leaching from TC-W-0.5 was much higher than that from TC-A-0.4. It is noteworthy that there was no significant change in the catalytic activity of TC-A-0.4 between the third and fourth runs, and that the leaching of TiO_2 was also very low (1%).

A TEM image of the reused TC-A-0.4 (second run) is shown in Fig. 8. Compared with fresh TC-A-0.4, the TiO_2 amount on the side wall of the o-MWCNTs had obviously decreased, whereas the TiO_2 density on the tip of the o-MWCNTs did not change for the reused TC-A-0.4. It is well known that the tip of CNTs possesses more oxygen containing functional groups than the side wall. These results indicated that the interactions between TiO_2 and the CNTs could be enhanced by the introduction of oxygen containing functional groups, which was consistent with the reusability test results. Furthermore, the specific surface area of the reused TC-A-0.4 (second run, 155 m^2/g) was slightly lower than that of the fresh one (161 m^2/g), which was attributed to the loss of TiO_2 .

Under the same reaction conditions, TC-A-0.4 showed much better reusability than the TiO_2/CNTs , which were prepared by depositing TiO_2 on the unmodified CNTs in the presence of a surfactant [27]. Furthermore, the reusability of TC-A-0.4 was better than that of other similar catalysts. For example, the activity of $\text{MoO}_3/\text{SiO}_2$ and $\text{TiO}_2/\text{SiO}_2$ was almost completely lost after they had been reused for four runs [20]. This result could be attributed to the interaction between TiO_2 and the CNTs being stronger than that between TiO_2 and the other inorganic supports.

Table 4
Reusability of TC-W-0.5 and TC-A-0.4

Catalyst	Run	Conversion of phenol (%)	Yield (%)		Loss of TiO_2^a (%)
			MPC	DPC	
TC-W-0.5	1	39.0	18.5	20.5	27
	2	28.7	15.0	13.7	16
	3	19.2	12.6	6.6	8
TC-A-0.4	1	39.5	17.9	21.6	12
	2	35.8	18.0	17.8	5
	3	33.5	17.7	15.8	3
	4	33.1	17.4	15.7	1
$\text{TiO}_2/\text{CNT}^{[27]}$	1	35.2	17.2	18.0	32
	2	16.8	9.5	7.3	25

Reaction conditions: DMC 0.16 mol, phenol 0.16 mol, TC-A-0.4 of 0.4 g (1.36% based on total material), 180 °C, 9 h.

^a The ratio of leached TiO_2 to total TiO_2 in the fresh catalyst.

Fig. 8. TEM image of the reused TC-A-0.4 (second run).

4. Conclusions

An efficient and easy to separate heterogeneous catalyst, $\text{TiO}_2/\text{o-MWCNT}$, has been prepared and used for the transesterification of DMC with phenol. The type and concentration of the precipitant had a remarkable effect on the activity, separability and reusability of $\text{TiO}_2/\text{o-MWCNTs}$. During the preparation of the $\text{TiO}_2/\text{o-MWCNTs}$, high levels of TiO_2 dispersion could be obtained by controlling the speed of the hydrolysis of the Ti precursor to form TiO_2 under a low concentration of the precipitant. The nucleation and growth of the TiO_2 occurred prior to the formation of the oxygen containing functional groups of the CNTs when ammonium hydroxide was used instead of deionized water as the precipitant, and this resulted in much easily to separate from the reaction mixture. When TC-A-0.4 was used as a catalyst, the conversion of phenol reached 42.5% with over 99.9% selectivity for MPC and DPC over 9 h, which could be reused for four runs with only a slight loss in its catalytic activity.

Acknowledgements

We thank Professor Mei-zheng Qu from Chengdu Organic Chemicals Co. Ltd. for providing MWCNT and helpful suggestions.

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Graphical Abstract

Chin. J. Catal., 2014, 35: 481–489 doi: 10.1016/S1872-2067(14)60010-3

Preparation and catalytic property of modified multi-walled carbon nanotube-supported TiO_2 for transesterification of dimethyl carbonate with phenol

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TiO_2 supported on modified multi-walled carbon nanotubes was prepared by controlling the hydrolysis rate of the titanium precursor. This material was then used as an efficient heterogeneous catalyst for the transesterification of dimethyl carbonate with phenol.

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表面修饰多壁碳纳米管负载二氧化钛的制备及催化碳酸二甲酯与苯酚酯交换反应的性能

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摘要: 制备了表面修饰多壁碳纳米管负载TiO₂的催化剂, 并将其应用于碳酸二甲酯与苯酚的酯交换反应. 采用X射线电子能谱、透射电子显微镜、低温N₂吸附-脱附和X射线衍射等对催化剂进行了表征. 结果表明, 以低浓度的氨水(0.4%)代替去离子水作为沉淀剂时, 制备的催化剂显示出更好的催化活性、分离性与重复使用性. 考察了TiO₂负载量、催化剂用量及反应时间对反应性能的影响. 在最佳反应条件下, 苯酚转化率为42.5%, 碳酸甲苯酯与碳酸二苯酯的总选择性达到99.9%以上. 经过4次重复使用后, 催化剂的活性略有下降.

关键词: 多壁碳纳米管; 二氧化钛; 碳酸二苯酯; 酯交换; 沉淀剂

收稿日期: 2013-11-07. 接受日期: 2013-12-24. 出版日期: 2014-04-20.

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基金来源: 国家高技术研究发展计划(863计划, SS2013AA031703); 四川省青年科技创新研究团队(2013TD0010).

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