



Studies on the carboxymethylation and methylation of bisphenol A with dimethyl carbonate over TiO₂/SBA-15

Kunmei Su^a, Zhenhuan Li^{a,*}, Bowen Cheng^{a,*}, Kun liao^a, Dexin Shen^a, Yufei Wang^b

^a College of Materials and Chemical Engineering, and Tianjin Key Lab of Fiber Modification & Functional Fiber, Tianjin Polytechnic University, Tianjin 300160, China

^b College of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

ARTICLE INFO

Article history:

Received 3 July 2009

Received in revised form 30 August 2009

Accepted 31 August 2009

Available online 6 September 2009

Keywords:

Carboxymethylation

Methylation

Dimethyl carbonate

Bisphenol A

TiO₂/SBA-15

ABSTRACT

Carboxymethylated species were selectively synthesized from dimethyl carbonate (DMC) and bisphenol A (BPA) over TiO₂/SBA-15. On the basis of catalyst characterization by means of XRD, FT-IR, HPLC and GC-MS, the relations between catalytic performance and catalyst properties were discussed. Si–O–Ti was active sites for reaction, and the interaction mode between Ti–O–Si and DMC was main factor to determine carboxymethylation and methylation. When DMC was attacked by Ti–O–Si on two oxygen atoms of CH₃–O moiety, BPA attacked carbonyl carbon to form carboxymethylated products. If the interaction occurs through the oxygen of C=O moiety, BPA attacked methyl carbon to form methylated products. Chemisorbed H₂O over TiO₂/SBA-15 made DMC to act as methylating agent. After chemisorbed H₂O was removed, carboxymethylated species of two-methylcarbonate-ended-BPA (DmC(1)) and one-methylcarbonate-ended-BPA (MmC(1)) were selectively synthesized.

© 2009 Elsevier B.V. All rights reserved.

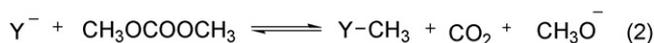
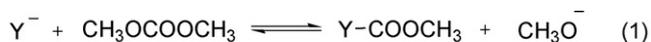
1. Introduction

Poly(bisphenol A carbonate) (PC) is an important thermoplastic which is often produced by the interfacial polycondensation of BPA and phosgene, however, phosgene process used highly toxic phosgene as the reagent and copious amounts of methylene chloride as the solvent [1]. Thus it is increasingly important that an environmentally friendly synthesis of PC is developed. In an attempt to devise a phosgene-free synthesis of PC, diphenyl carbonate (DPC) [1–6], CO [7–13] and DMC [14–18] were used as carbonylating agents to replace phosgene. The reaction between DPC and BPA resulted in phenol as a condensation byproduct, but phenol removing often took place under the conditions of rising temperature (higher than 300 °C) and lowering vacuum pressure (less than 13 Pa). However, these severe reaction conditions easily result in fatal damages to the PC produced, such as the thermal instability of BPA at high temperature can result in the discoloration of the final product and complicated byproducts [19]. As a potential substitute for DPC, DMC would react with BPA into polycarbonate precursors, and it has a great advantage that there is no need to obtain DPC. Furthermore, polycondensation steps of the prepolymers removing methanol often took place under lower temperature.

Shaikh et al. [14] and Habu et al. [18] reported that the methylcarbonate-ended oligomers were most reactive in producing high molecular weight polymers in the postpolycondensation step compared with hydroxyl-ended oligomers. Therefore, the selective synthesis of methylcarbonate-ended oligomers became most important. However, the presence of two nonequivalent electrophilic centers in DMC, the carbonyl and methyl moieties, make it possible for BPA nucleophile to undergo methylation and carboxylation [20]. Methylation products of BPA are unreactive in the postpolymerization step because they have no carbonate functional end groups to react further. Therefore, minimization of methylation byproducts is indispensably required. The central carbon of DMC, due to sp² hybridization, results in a greater positive charge of the carbon atom, making it a harder center. The two methyl groups on the other hand are the softer electrophilic centers, owing to the acceptor atom having an sp³ orbital and a saturated carbon atom, which has a weaker positive charge [21]. Therefore, in an extension of Pearson's HSAB theory [22], it is possible to say that harder nucleophiles in a reaction with DMC will undergo carboxymethylation (hard reaction, Scheme 1, reaction 1), while softer nucleophiles will undergo methylation (soft reaction, Scheme 1, reaction 2). As for phenols with an electron withdrawing group (EWG) and phenols with electron donating groups (EDG), an EWG would make the phenolic oxygen more polarizable, making it a softer donor atom. Contrarily, an EDG would decrease the polarizability of the donor atom, making the phenolic oxygen a harder donor atom [21]. It could be speculated that harder BPA nucleophile in a reaction with DMC will mainly underwent carboxymethylation.

* Corresponding authors. Tel.: +86 222452 8358; fax: +86 222452 8055.

E-mail addresses: zhenhuanli1975@yahoo.com.cn (Z. Li), Bowen15@tjpu.edu.cn (B. Cheng).



Scheme 1. (1) Carboxymethylation and (2) methylation reactions.

Carboxymethylation of BPA with DMC was often catalyzed by Lewis acid catalysts, for example, $\text{TiO}_2/\text{SiO}_2$ [23], $(\text{Bu}_2\text{SnCl})_2\text{O}$ [18], Bu_2SnO and titanium alkoxides. Haba et al. [18] reported the synthesis of methylcarbonate-ended oligomers from the carboxymethylation of BPA with a large excess of DMC (68 times the mole of initial BPA), methylcarbonate-ended oligomers could be produced with 22% yield with respect to BPA converted after 48 h under a catalyst system of dibutyltinchlorooxide and dimethylaminopyridine. Also, they used a substantial amount of a 4 Å molecular sieve (3.5 times the weight of initial BPA) to remove the methanol coproduced to alleviate the equilibrium limitation. Because the separation of homogeneous catalyst from products was complicated, the development of heterogeneous catalysts with better activity and higher selectivity was highly desirable in view of regeneration and separation. However, there are few reports on the development of active heterogeneous catalysts for this reaction.

The ordered mesoporous silicas like SBA-15 [24] and MCM-41 [25,26], with adjustable pore sizes, very high specific surface areas and large pore volume, provided a special platform for the development of advanced materials with different chemical functionalities [27–29]. Substitution of Si by Ti created more attention, and the conventional way to introduce Ti in mesoporous silicas was usually achieved by direct synthesis. Postsynthetic incorporation of Ti in mesoporous silicates is much less investigated; however, the postsynthetic incorporation of Ti seems to have a great advantage, that is, the opportunity to start with a highly ordered mesoporous material with a very high inner surface and pore volume. Herein, the carboxymethylation of BPA with DMC was promoted by $\text{TiO}_2/\text{SBA-15}$ which was prepared by postsynthetic process. Si–O–Ti was active sites for reaction, and the interaction mode between Ti–O–Si and DMC was main factor to determine carboxymethylation and methylation. Chemisorbed water blocked the carboxymethylation, and 10 wt% $\text{TiO}_2/\text{SBA-15}$ gave the best results to produce MmC(1) and DmC(1) in 25.3% and 3.6% yields at 10 h. In addition, the effects of TiO_2 loading, temperature, time, catalyst amount, phenol/DMC mole ratio on reaction were investigated, and possible reaction mechanism was provided.

2. Experiments

2.1. Chemical reagents

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was purchased from Tianjin Chemical Reagent Co. (IV) and used as received. DMC (Tianjin Chemical Reagent Research Institute) was fractionally distilled and stored over molecular sieve (4 Å). Tetrabutoxy titanium (TBOT) was purchased from Tianjin Kermel Chemical Reagents Development Center. BPA (Tianjin Chemical Reagent Co. (III)) was of analytic reagent (AR) grade and used without further purification. Other chemical reagents were AR grade and used as received from local manufactures without further purification.

2.2. Sample preparation

SBA-15 was synthesized in accordance with the published procedure [30] using tri-block copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) [$(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$] as template in acidic conditions. In brief, a solution of

$(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20} \cdot \text{HCl} : \text{TEOS} : \text{H}_2\text{O} = 2:60:4.5:15$ (mass ratio) was prepared, stirred for 24 h at 40 °C, and then heated under autogenous pressure in a sealed autoclave at 100 °C for 24 h. The solid product was collected by filtration and calcined at 550 °C for 6 h. To prepare $\text{TiO}_2/\text{SBA-15}$ catalysts, SBA-15 was impregnated in ethanol solution of TBOT at room temperature for 24 h, and then dried in an oven at 80 °C for 8 h to remove ethanol. The TBOT-impregnated silica was calcined with an air stream at 550 °C for 3 h. Other metal oxides were loaded on SBA-15 supports by the wet impregnation of corresponding metal nitrate. After solvent was removed by evaporation at 80 °C for 8 h, the catalysts were calcined at 550 °C for 3 h.

2.3. Characterization

XRD patterns were measured on a Bruker AXS (Germany) using $\text{Cu K}\alpha$ radiation. The data was recorded from 1° to 80° (2 θ). FT-IR spectrum was obtained on a Nicolet Nexus 470 FT-IR analyzer using the KBr method. Reaction products were analyzed by HPLC and GC–MS (HP5972) (capillary column: 30 m SE-30, 0.25 mm ID, and 0.25 μm film thickness) to identify products and polycarbonate precursors. Quantitative analysis was carried on a gas chromatograph (Agilent 6890N GC with a FID detector, HP-5/DB-5 capillary column) with cetane as interior standard. The HPLC analyses were carried out by a reverse-phase method on a Waters 2690 separation module (Waters Associates, Milford, MA). As an UV detector, a Waters 2487 Dual Absorbance Detector was used at the wavelength of UV 240 nm. The reverse-phase LC column was Waters Lichrosorb RP18 analytical column. A mobile phase flow rate of 1 mL/min was adjusted with a gradient mode of acetonitrile and water from 65/35 to isocratic of acetonitrile. The reaction samples were diluted with THF and 5 μL was injected. The Millennium 32 software was used for data reduction and integration. It gave a good separation and UV sensitivity to polycarbonate precursors and BPA.

2.4. Reaction procedure

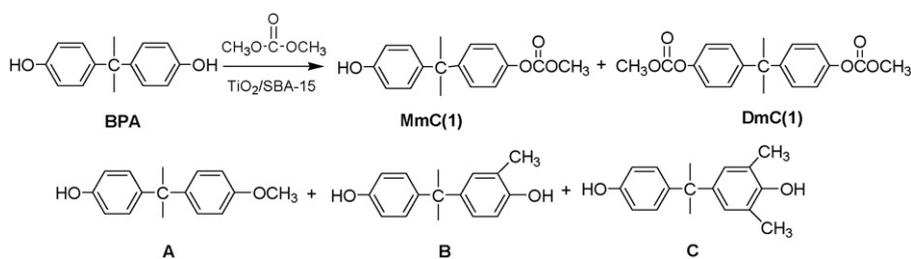
Reactions were carried out in a four neck flask, equipped with a thermometer, nitrogen inlet, dropping funnel and fractionating column connected to a liquid dividing head. BPA and catalyst were charged into flask under nitrogen atmosphere. When mixture was heated to 160 °C, DMC was added drop-wise, and reaction was continued for a certain period of time. During the reaction, a distillate of DMC and methanol was collected slowly in a receiver flask. After reaction finished, mixture was cooled and analyzed. DmC(1) and DmC(1) yields were based on initial BPA.

3. Results and discussion

The carboxymethylation of BPA with DMC mainly produced MmC(1) and DmC(1), and heavier products from further reaction of MmC(1) and DmC(1) were not detected by HPLC analyses, unlike in the case of BPA and DPC. In addition, there were little byproducts formed from O-methylation of BPA (A), ortho-methylation of BPA with DMC (B and C) (see Scheme 2).

3.1. The effects of various catalysts on carboxymethylation and methylation

As shown in Table 1, $\text{TiO}_2/\text{SBA-15}$ showed highest activities among TiO_2 nanoparticle, $\text{MoO}_3/\text{SBA-15}$, $\text{ZnO}/\text{SBA-15}$ and $\text{Pb}_2\text{O}_3/\text{SBA-15}$. MmC(1) and DmC(1) could be produced with 25.3% and 3.6% yields with respect to BPA converted over $\text{TiO}_2/\text{SBA-15}$ at 10 h. Reutilization catalytic test indicated that $\text{RTiO}_2/\text{SBA-15}$ could be reused and showed even higher activity for DmC(1) synthesis. When TiO_2 nanoparticle acted as catalyst, MmC(1) and DmC(1)



Scheme 2. The reaction of BPA and DMC over TiO₂/SBA-15.

yields declined to 7.4% and 1.2%. Although MoO₃ and Pb₃O₄ supported catalyst displayed the high activity in reaction between DMC and phenol [26,31], no DmC(1) was detected, and only 9.1% and 3.4% MmC(1) yields were obtained over MoO₃/SBA-15 and Pb₃O₄/SBA-15. When reaction was carried out over ZnO/SBA-15, the selectivity of carboxymethylated byproducts amounted to 41.7%. The main difference in the two catalytic reactions of ZnO/SBA-15 and TiO₂/SBA-15 was the relative percentages of carboxymethylation and methylation at the completion of reaction, signifying that ZnO/SBA-15 has great effect on the hard–soft behavior of this class of nucleophile. Although (C₄H₉)₂SnO showed the high activity in carboxymethylation, it belonged to homogeneous catalysts which resulted in difficult separation of catalysts from products. Considering the stability and facile recovery and regeneration after reaction, silica-supported titania was chosen as better catalyst.

The investigation of heterogeneous catalyst framework was conducted via FT-IR spectroscopy, and results were shown in Fig. 1. TiO₂/SBA-15 showed a strong absorption peak at 960 cm⁻¹ that could be ascribed to the vibration of O₃–Si–O–Ti in supported molecular sieve [32]. The bands at 800 cm⁻¹ and 1090 cm⁻¹ were for symmetric Si–O–Si stretching vibration and asymmetric Si–O–Si stretching vibration, respectively. IR bands at 1630 cm⁻¹ and 3450 cm⁻¹ were attributed to bending vibration and stretching vibration of the O–H bond of chemisorbed H₂O on Lewis acid sites [33]. The characterized results indicated that the Si–O–Ti species over TiO₂/SBA-15 had high activity for carboxymethylation of BPA with DMC.

Ti–O–Si has tetrahedral symmetry of Ti with four surrounding O anions [34], so DMC adsorbs preferentially the surface Ti–O–Si bonds to form cis–cis and cis–trans species together with tetrahedral Ti changing into octahedral Ti with six surrounding O anions (I) or pentahedral Ti with five surrounding O anions (II and III) (see Scheme 3) [35]. When the interaction between Ti–O–Si and DMC occurs through the two oxygen atoms of the CH₃–O moiety, the electrostatic perturbation in adducts Ti–O–Si and DMC with cis–cis species (I) induces an elongation (weakening) of the C–OCH₃ bonds, a fact which can explain the high catalytic activity of TiO₂/SBA-15 in carboxymethylation reactions. If the interaction between Ti–O–Si and DMC occurs through the oxygen of the C=O moiety, in adducts

Table 1
Effects of catalyst on carboxymethylation and methylation.

Catalyst	Product distribution (mol%)			YMmC(1) (mol%)	YDPC(1) (mol%)
	MmC(1)	DmC(1)	Methylation products		
TiO ₂	80.5	12.6	6.9	7.4	1.2
TiO ₂ /SBA-15	83.4	11.7	4.9	25.3	3.6
RTiO ₂ /SBA-15	81.2	13.5	5.3	23.4	3.9
MoO ₃ /SBA-15	99.0	–	1.0	9.1	–
ZnO/SBA-15	58.3	–	41.7	4.2	–
Pb ₃ O ₄ /SBA-15	91.8	–	8.2	3.4	–
(C ₄ H ₉) ₂ SnO	80.5	18.1	1.4	44.3	10.0

Reaction conditions: BPA 11.4 g, DMC 18 g, catalyst 0.5 g (with 10 wt% metal oxide loading), 160 °C, 10 h. RTiO₂/SiMCM-41 is the secondly used catalyst which is activated at 550 °C for 3 h.

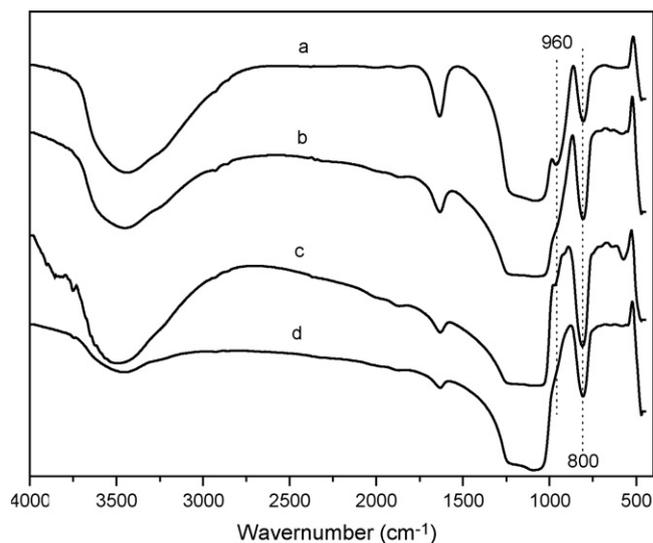
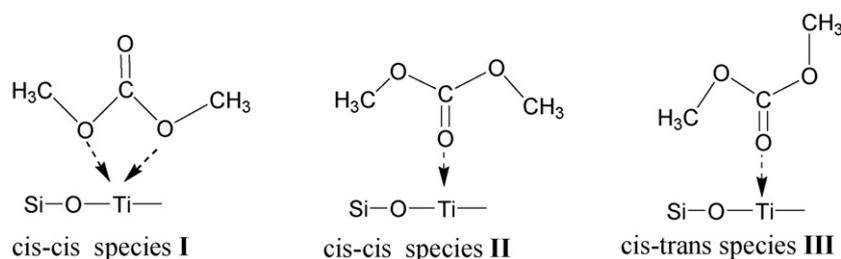


Fig. 1. FT-IR of supported catalyst (a) TiO₂/SBA-15, (b) ZnO/SBA-15, (c) MoO₃/SBA-15, and (d) Pb₂O₃/SBA-15.

Ti–O–Si and DMC with cis–cis and cis–trans species (II and III) an elongation of the O–CH₃ bonds occurs, which justifies the catalytic activity of TiO₂/SBA-15 in methylation reactions. When DMC adsorbed the surface ZnO/SBA-15, much the interaction occurs through the oxygen of the C=O moiety, which could explain the selectivity of methylation byproducts amounted to 41.7%.

3.2. Effect of TiO₂ loading on carboxymethylation and methylation

The X-ray powder diffraction analysis was undertaken to determine the composition and crystallinity of Ti species. The low-angle XRD patterns of TiO₂/SBA-15 were displayed in Fig. 2(a). The well-defined diffraction peak indexable as 100 reflection, which was associated with SBA-15 type mesostructures, was observed for all these samples. The peak intensity was almost kept with an increase in TiO₂ loading up to 30 wt%, suggesting that the long-



Scheme 3. DMC adsorbs the surface Ti–O–Si bonds to form cis–cis and cis–trans species. Tetrahedral Ti with four surrounding O anions transfer into octahedral Ti with six surrounding O anions (I) and pentahedral Ti with five surrounding O anions (II and III).

range regularity of hexagonal arrays of mesopores was sustained after the introduction of TiO_2 by wet impregnation technique. However 110 and 200 reflections decreased as TiO_2 loading increasing, which suggested that TiO_2 species deposited inside the mesopore channels. The extensive-angle XRD showed that there were no characteristic diffraction peaks of TiO_2 crystal when the loading amount of TiO_2 was less than 10 wt%. When TiO_2 loading increased to 20 wt%, the XRD peaks of anatase TiO_2 crystal appeared, which showed the presence of bulk titanium oxide crystal on catalyst surface.

The FT-IR spectra of catalysts were listed in Figs. 3 and 4. The broad absorption band for OH stretching around 3400 cm^{-1} and the corresponding HOH bending at 1630 cm^{-1} occurred [33]. As TiO_2 loading increasing, the absorption band at 960 cm^{-1} became stronger. The stronger absorption peaks at 960 cm^{-1} indicated the more titanium was incorporated into SBA-15 framework, i.e., much more Si–O–Ti species existed over $\text{TiO}_2/\text{SBA-15}$ [32]. 639 cm^{-1} suggested that Ti–O–Ti species appear on $\text{TiO}_2/\text{SBA-15}$. It was worthy of noting that there were two weak absorption peaks at 2336 cm^{-1} and 2360 cm^{-1} in 10 wt% $\text{TiO}_2/\text{SBA-15}$. Those two weak bands were attributed to vibration of chemisorbed CO_2 over defect sites which were mainly caused by O vacancies [36] and tetrahedral environment [37,38]. It was well known that Ti–O–Si species have tetrahedral symmetry of Ti with four surrounding O anions [34] and tetrahedral TiO_4 has been thought to be important to cat-

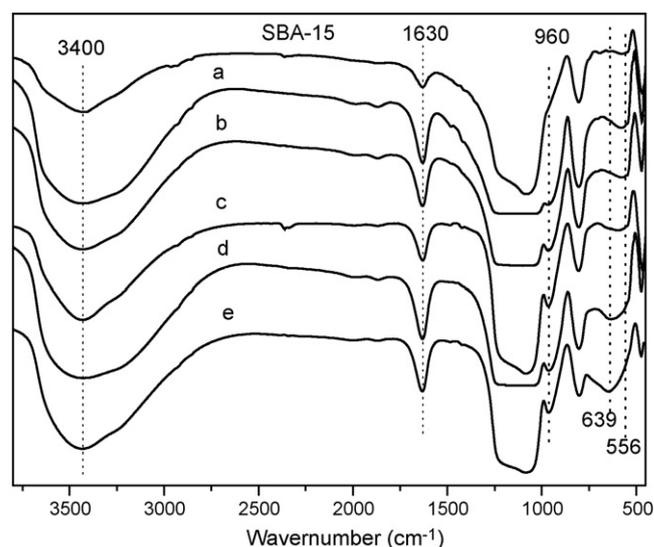


Fig. 3. FT-IR of $\text{TiO}_2/\text{SBA-15}$ with different TiO_2 loadings: (a) 2.5 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%, and (e) 30 wt%.

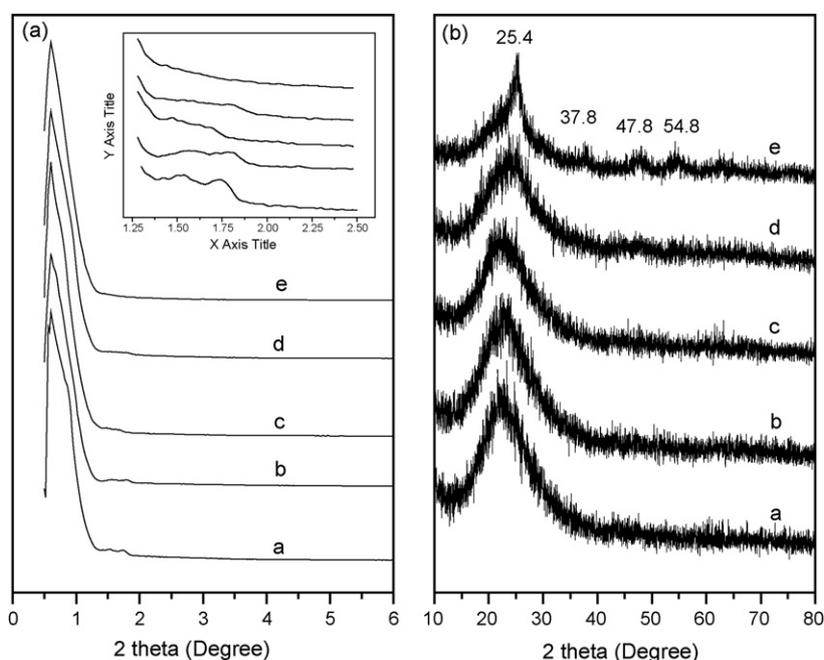


Fig. 2. XRD patterns of $\text{TiO}_2/\text{SBA-15}$ with different TiO_2 loadings at small-angle and extent-angle: (a) 2.5 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%, and (e) 30 wt%.

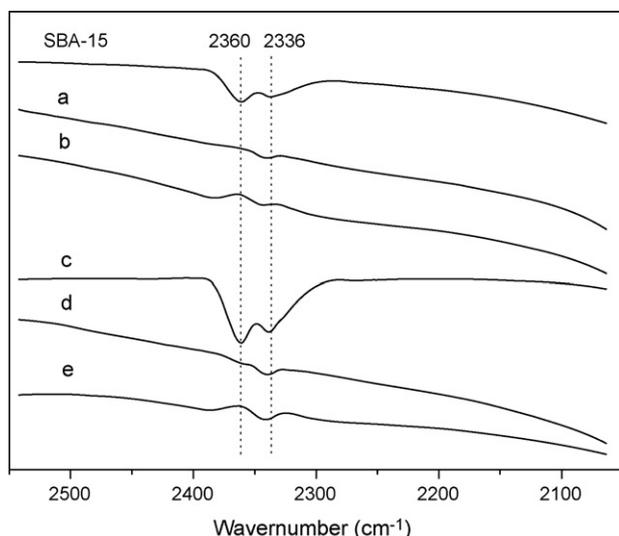


Fig. 4. FT-IR of $\text{TiO}_2/\text{SBA-15}$ with different TiO_2 loadings: (a) 2.5 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%, and (e) 30 wt%.

alytic applications because it is attributed to the active center of many reactions [39]. The structure defect in 10 wt% $\text{TiO}_2/\text{SBA-15}$ was mainly caused by the appearance of more Si–O–Ti species in Ti–Si binary oxides [34].

The effects of TiO_2 loading on reaction were shown in Fig. 5. When 2.5 wt% $\text{TiO}_2/\text{SBA-15}$ was used as catalyst, no DmC(1) was detected, and MmC(1) yield was 6.4%, however, methylation product selectivity achieved the maximum 15.8%. When TiO_2 loading amounted to 5 wt%, DmC(1) yield achieved 0.32%, and MmC(1) yield increased to 8.8%. The maximum DmC(1) yield of 0.54% and minimum methylation product selectivity of 2.3% were obtained over catalyst with 10 wt% TiO_2 loading. When reaction was catalyzed by 30 wt% $\text{TiO}_2/\text{SBA-15}$, DmC(1) yield decreased to 0.34%, while methylation product selectivity increased to 8.0%, respectively. The reason for the high activity of 10 wt% $\text{TiO}_2/\text{SBA-15}$ for DmC(1) synthesis might be that much more Si–O–Ti species existed on surface of 10 wt% $\text{TiO}_2/\text{SBA-15}$, and the electrophilic interaction of DMC was augmented by Ti cation in Si–O–Ti species.

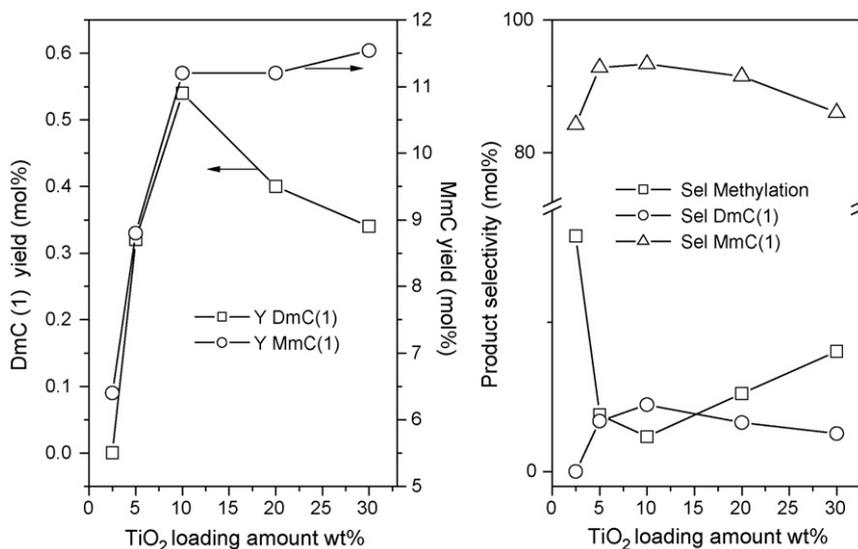


Fig. 5. Effect of TiO_2 loading on carboxymethylation and methylation (reaction condition: BPA 5.7 g, DMC 9 g, catalyst 0.5 g, 180 °C, 6 h).

3.3. Effect of reaction temperature on carboxymethylation and methylation

As shown in Fig. 6, no DmC(1) was detected at 140 °C even after 10 h, and only 1.2% MmC(1) yield was obtained, however, methylation product selectivity achieved 88.3%. When reaction was carried out at 160 °C, MmC(1) and DmC(1) yields achieved 0.8% and 13.6%, and methylation product selectivity declined to 7.7%. Furthermore, if reaction was carried out at 200 °C, MmC(1) and DmC(1) yield increased to 4.6% and 21.1%, together with methylation product selectivity further decline to 4.5%.

The yield of DmC(1) and MmC(1) increases as temperature increasing, while the methylated product selectivity decreased. Those behaviors could be explained by two effects: (1) When reaction was carried at high temperature, the coproduced methanol was separated easily by distillation, which alleviated the equilibrium limitation of the reaction between BPA and DMC. (2) Another problem is the effect of water adsorption from ambient humidity. Hydration could break Ti–O–Si bridging bonds exposed to the surface to form Ti–OH hydroxyls which are a five-coordinated Ti species [40]. The interaction between five-coordinated Ti species and DMC occurred through the oxygen of the C=O moiety, which lead to high selectivity to methylation. If reaction was carried out at 140 °C, heat activation may not ensure the complete absence of chemisorbed water on catalyst surface [41]. When reaction was carried out at 160 °C, water molecules were removed from $\text{TiO}_2/\text{SBA-15}$. Only when the chemisorbed water is completely removed, the high selectivity to carboxymethylation reactions might occur.

3.4. Effect of reaction time on carboxymethylation and methylation

A further study was carried out to investigate the equilibrium conversion of BPA over 10 wt% $\text{TiO}_2/\text{SBA-15}$ with an extended reaction time of 12 h. As shown in Fig. 7, DmC(1) yield increased from 0% to 2.74% as reaction time increasing from 2 h to 12 h, and DmC(1) selectivity showed an almost linear increase with time prolonging, and it amounted to 16.4% at 12 h. MmC(1) yield achieved 13.2% and its selectivity obtained 79.1% at 12 h. Carboxymethylation commonly proceeded by a condensation reaction (see Scheme 4), in which methanol was eliminated in each step. As reaction time

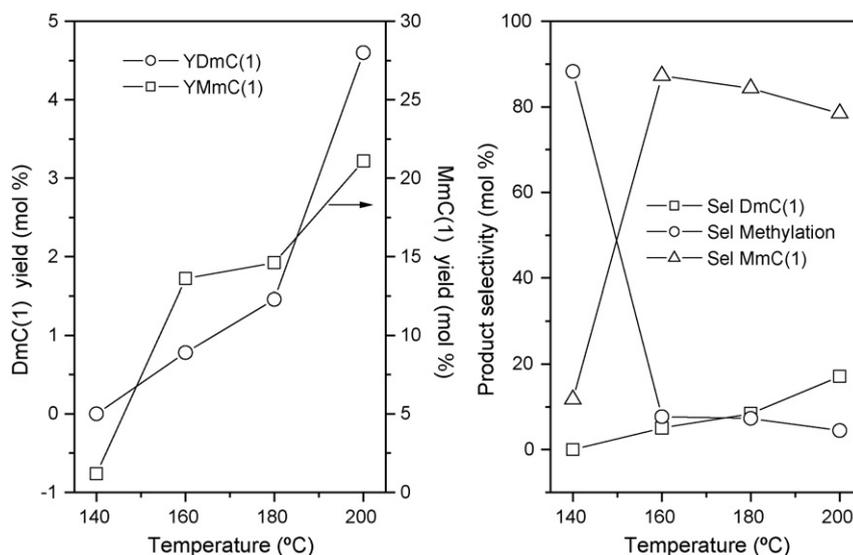


Fig. 6. Effect of reaction temperature on carboxymethylation and methylation (reaction conditions: BPA 11.4 g, DMC 18 g, 10 wt% TiO₂/SBA-15 0.5 g, 10 h).

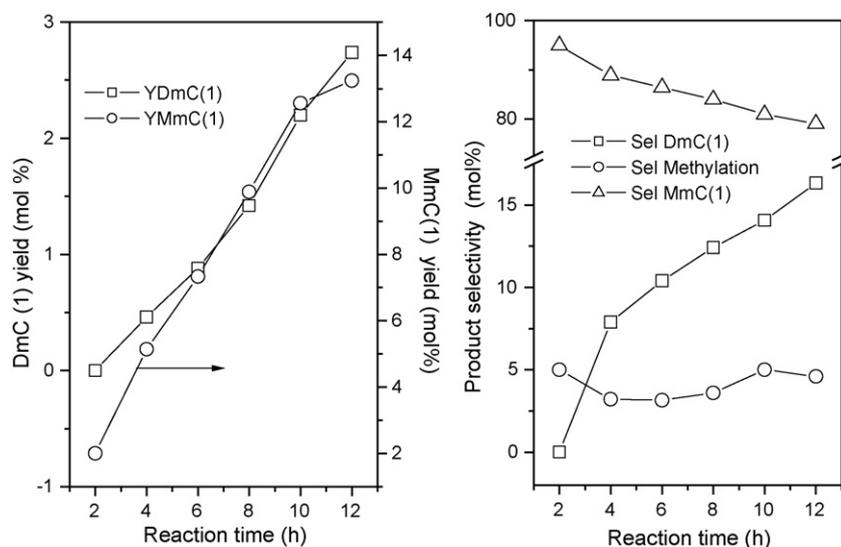


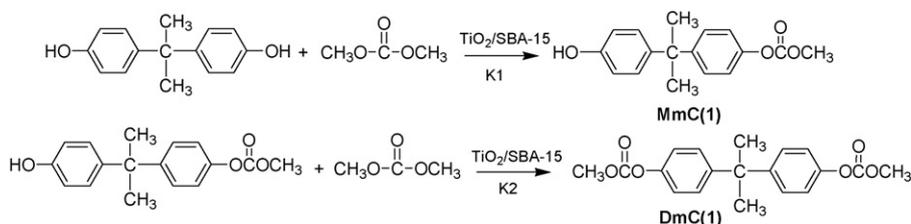
Fig. 7. Effect of reaction time on carboxymethylation and methylation (reaction conditions: BPA 11.4 g, DMC 18 g, 10 wt% TiO₂/SBA-15 0.5 g, 160 °C, 10 h).

extended to remove methanol, the equilibrium limitation of reaction was alleviated.

3.5. Effect of catalyst usage amount on carboxymethylation and methylation

In order to improve DmC(1) yield, the influence of catalyst usage amount was investigated, and results were shown in Fig. 8. When the amount of catalyst usage was 0.25 g, the yields of MmC(1) and DmC(1) were 5.6% and 0.44%. As the amount of

catalyst usage increased to 0.75 g, MmC(1) and DmC(1) yields increased to 10.4% and 0.64%, while methylated product selectivity achieved the minimum 3.0%. When 1.0 g catalyst was used, no DmC(1) was obtained, and MmC(1) yield was only 1.9%, while methylated product selectivity achieved 11.8%, which might be caused by TiO₂/SBA-15 powder deposition at flask bottom to influence thermal conductivity. However, when 0.75 g catalyst was used, the presence of suspended TiO₂/SBA-15 nanosized solid particles in solution exhibited the effective thermal conductivity [42,43].



Scheme 4. The carboxymethylation of BPA with DMC over TiO₂/SBA-15.

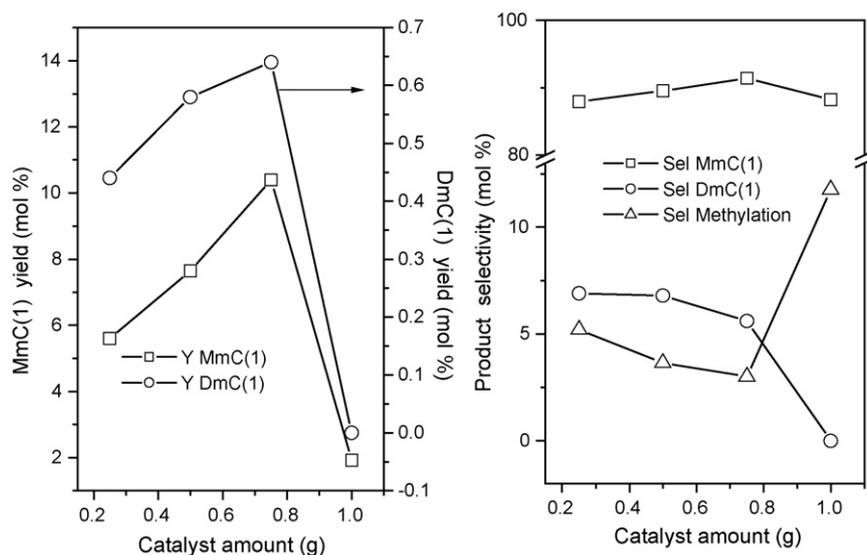


Fig. 8. Effect of 10 wt% TiO₂/SBA-15 amount on carboxymethylation and methylation (reaction conditions: BPA 11.4 g, DMC 18 g, 180 °C, 10 h).

3.6. Effect of DMC/BPA mole ratio on carboxymethylation and methylation

Effect of DMC/BPA mole ratio on carboxymethylation and methylation was investigated over 10 wt% TiO₂/SBA-15, as shown in Fig. 9. When reactions were carried out at 180 °C, MmC(1) yield increased from 4.8% to 23.8% and DmC(1) yield increased from 0.3% to 2.9% as the mole ratio of DMC to BPA increasing from 2 to 6. However, when the molar ratio of DMC to BPA increased to 8, DmC(1) and MmC(1) yields declined to 0.12% and 8.68%. The maximum DmC(1) selectivity of 10.8% was obtained when the mole ratio of DMC to BPA reached 6. The methylated product selectivity showed linear decrease from 4.5% to 0.5% as the mole ratio of DMC to BPA increasing from 2 to 8. It was worthy of noting that when the mole ratio of DMC to BPA was 2 and 4, DmC(1) yields were only 0.3% and 0.58%.

3.7. Suggested mechanism

In the reaction between DMC and BPA over TiO₂/SBA-15, DMC was attacked by Ti–O–Si on two oxygen atoms of the CH₃–O moiety, which increased the positive character of its carbonyl group, and the electrostatic perturbation in adducts Ti–O–Si and DMC with cis–cis species (I) induces an elongation (weakening) of the C–OCH₃ bonds. Therefore, the oxygen of BPA mainly attacked the carbonyl carbon to form the tetrahedral intermediate (Scheme 5). H transferred from OH to the tetrahedral intermediate on one of its methoxyl oxygens, and then DmC(1) or MmC(1) formed. This process can explain the high catalytic activity of TiO₂/SBA-15 in carboxymethylation reactions. If the interaction occurs through the oxygen of the C=O moiety, in adducts Ti–O–Si and DMC with cis–cis and cis–trans species (II and III) an elongation of the O–CH₃ bonds occurs, and then the oxygen of BPA mainly attacked the methyl carbon to form methylated products.

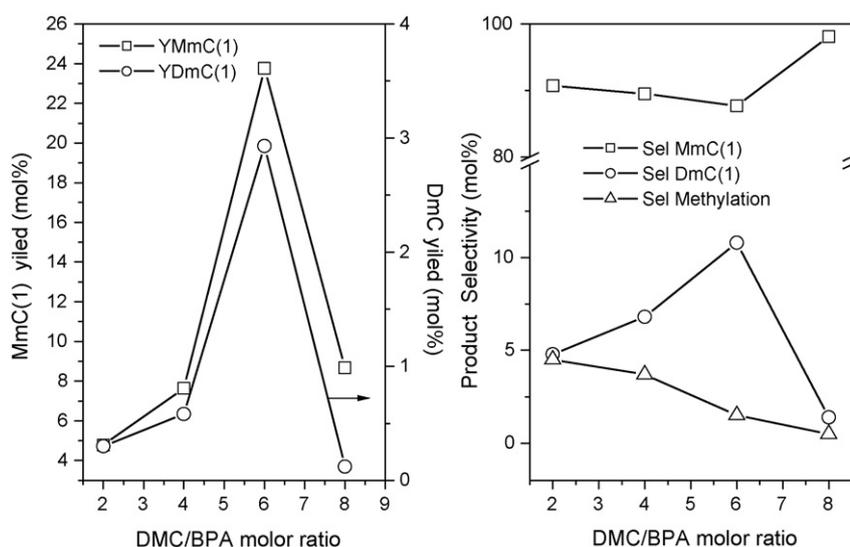
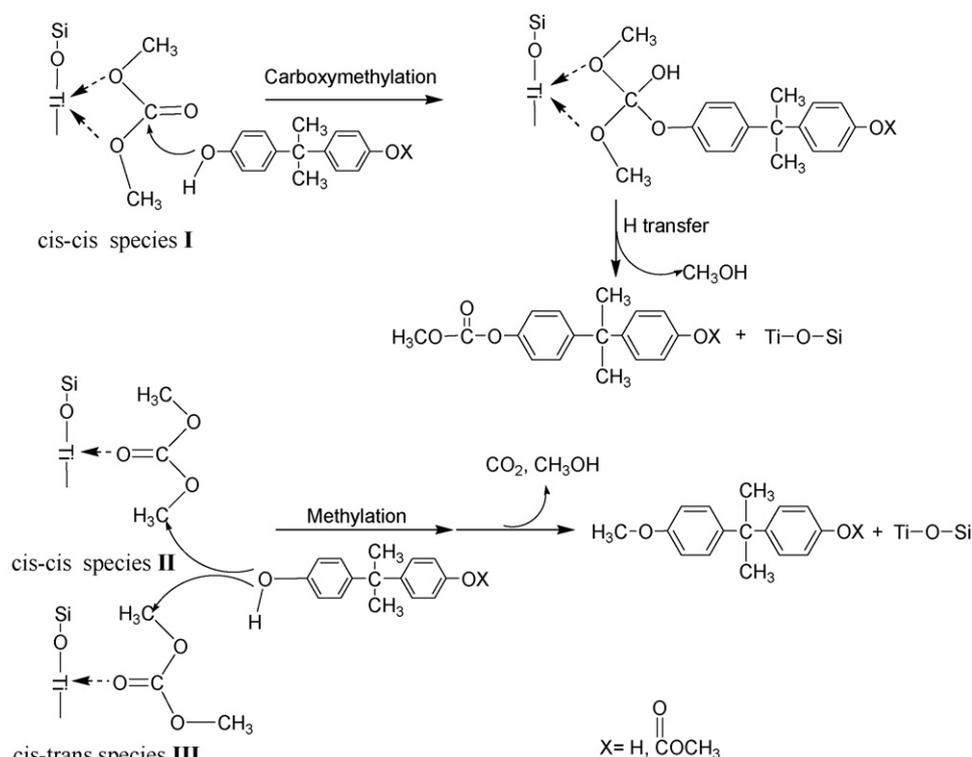


Fig. 9. Effect of DMC/BPA mole ratio on carboxymethylation and methylation (reaction conditions: BPA 11.4 g, 10 wt% TiO₂/SBA-15 0.5 g, 180 °C, 10 h).



Scheme 5. The process of the carboxymethylation and methylation of BPA with DMC over TiO₂/SBA-15.

4. Conclusions

The reaction between BPA and DMC was promoted by TiO₂/SBA-15. An appropriate amount of TiO₂ (10 wt%) supported on SBA-15 gave the best results to produce MmC(1) and DmC(1) in 25.3% and 3.6% yields at 10 h. The species of Si–O–Ti was activity sites for reaction, and the interaction mode between Ti–O–Si and DMC was main factor to determine carboxymethylation and methylation reactions. DMC was attacked by Ti–O–Si on two oxygen atoms of the CH₃–O moiety, and the oxygen of BPA attacked the carbonyl carbon to form carboxymethylated products. If the interaction occurs through the oxygen of the C=O moiety, and then the oxygen of BPA attacked the methyl carbon to form methylated products. When reaction was carried out at 140 °C, heat activation might not ensure the complete absence of chemisorbed H₂O on catalyst surface. Only when the chemisorbed H₂O was completely removed, high selectivity to carboxymethylation reactions could take place. The presence of suspended TiO₂/SBA-15 nanosized solid particles in solution exhibited the effective thermal conductivity, which led to higher DmC(1) and MmC(1) yields. When reaction was carried at high temperature, the coproduced methanol was separated easily by distillation, which alleviated the equilibrium limitation of the reaction between BPA and DMC. However, high reaction temperature resulted in less DMC coexisted in solution, and too much DMC loaded often debased the reaction temperature.

Acknowledgments

The authors are grateful for the financial support of the Natural Science Foundation of Tianjin Technolgy and Science Committee (09JCYBJC03000) and the Natural Science Foundation of Tianjin Education Committee (20070607).

References

- [1] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, *Green Chem.* 5 (2003) 497.
- [2] E. Turska, A.M. Wrobel, *Polymer* 11 (1970) 415.
- [3] Y. Kim, K.Y. Choi, T.A. Chamberlin, *Ind. Eng. Chem. Res.* 31 (1992) 2118.
- [4] S.N. Hersh, K.Y. Choi, *J. Appl. Polym. Sci.* 41 (1990) 1033.
- [5] Y. Kim, K.Y. Choi, *J. Appl. Polym. Sci.* 49 (1993) 747.
- [6] U. Curtius, L. Bottoenbruch, H. Schnell, U.S. Patent 3,442,854 (1969).
- [7] M. Goyal, R. Nagahata, J. Sugiyama, M. Asai, M. Ueda, K. Takeuchi, *Polymer* 40 (1999) 3237.
- [8] J.E. Hallgren, G.M. Lucas, R.O. Mathews, *J. Organomet. Chem.* 204 (1981) 135.
- [9] I.I. Moiseev, M.N. Vargaftik, T.V. Chernysheva, T.A. Stromnova, A.E. Gekhman, G.A. Tsirkov, A.M. Makhlina, *J. Mol. Catal. A* 108 (1996) 77.
- [10] M. Goyal, R. Nagahata, J. Sugiyama, M. Asai, M. Ueda, K. Takeuchi, *J. Mol. Catal. A* 137 (1999) 147.
- [11] M. Takagi, H. Miyagi, T. Yoneyama, Y. Ohgomori, *J. Mol. Catal. A* 129 (1998) L1.
- [12] H.Y. Song, E.D. Park, J.S. Lee, *J. Mol. Catal. A* 154 (2000) 243.
- [13] H. Ishii, M. Goyal, M. Ueda, K. Takeuchi, M. Asai, *J. Mol. Catal. A* 148 (1999) 289.
- [14] A.G. Shaikh, S. Sivaram, C. Puglisi, F. Samperi, G. Montaudo, *Polym. Bull.* 32 (1994) 427.
- [15] V. Pokharkar, S. Sivaram, *Polymer* 36 (1995) 4851.
- [16] M.M. Deshpande, A.S. Jadhav, A.A. Gunari, J.C. Sehra, S. Sivaram, *J. Polym. Sci. Part A: Polym. Chem.* 33 (1995) 701.
- [17] D.A. Bolon, J.E. Hallgren, U.S. Patent 4,452,968 (1984).
- [18] O. Haba, I. Itakura, M. Ueda, S. Kuze, *J. Polym. Sci. Part A: Polym. Chem.* 37 (1999) 2087.
- [19] H. Schnell, *Chemistry and Physics of Polycarbonates*, John Wiley, New York, 1964, p. 48.
- [20] A.E. Rosamilia, F. Aricò, P. Tundo, *J. Phys. Chem. B* 112 (2008) 14529.
- [21] P. Tundo, L. Rossi, A. Loris, *J. Org. Chem.* 70 (2005) 2219.
- [22] R.G. Pearson, *J. Am. Chem. Soc.* 85 (1963) 3533.
- [23] W.B. Kim, Y.G. Kim, J.S. Lee, *J. Appl. Polym. Sci.* 86 (2002) 937.
- [24] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Frederickson, B.F. Chmelka, G.D. Stucky, *Science* 279 (1998) 548.
- [25] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [26] Z. Li, B. Cheng, K. Su, Y. Gu, P. Xi, M. Guo, *J. Mol. Catal. A* 289 (2008) 100.
- [27] F. Schüth, W. Schmidt, *Adv. Eng. Mater.* 4 (2002) 269.
- [28] D. Brunel, A.C. Blanc, A. Galarneau, F. Fajula, *Catal. Today* 73 (2002) 139.
- [29] L.M. Bronstein, *Top. Curr. Chem.* 226 (2003) 55.
- [30] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.

- [31] W. Zhou, X. Zhao, Y. Wang, J. Zhang, *Appl. Catal. A* 260 (2004) 19.
- [32] G.N. Vayssilov, *Catal. Rev. Sci. Eng.* (1997) 209.
- [33] M. Zhang, L. Shi, S. Yuan, Y. Zhao, J. Fang, *J. Colloid Interface Sci.* 330 (2009) 113.
- [34] W.B. Kim, S.H. Choi, J.S. Lee, *J. Phys. Chem. B* 104 (2000) 8670.
- [35] F. Bonino, A. Damin, S. Bordiga, M. Selva, P. Tundo, A. Zecchina, *Angew. Chem. Int. Ed.* 44 (2005) 4774.
- [36] S. Wendt, P.T. Sprunger, E. Lira, G.K.H. Madsen, Z. Li, J.Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, F. Besenbacher, *Science* 320 (2008) 1755.
- [37] W.B. Kim, J.S. Lee, *J. Catal.* 185 (1999) 307.
- [38] W.B. Kim, Y.G. Kim, J.S. Lee, *Appl. Catal. A* 194/195 (2000) 403.
- [39] H. Yoshitake, T. Sugihara, T. Tatsumi, *Chem. Mater.* 14 (2002) 1023.
- [40] X. Gao, S.R. Bare, J.L.G. Fierro, M.A. Banares, I.E. Wachs, *J. Phys. Chem. B* 102 (1998) 5653.
- [41] P. Tundo, F. Aricò, A.E. Rosamili, S. Memolia, *Green Chem.* 11 (2008) 1182.
- [42] H.C. Li, G.P. Peterson, *J. Appl. Phys.* 101 (2007) 044312.
- [43] A. Amrollahi, A.A. Hamidi, A.M. Rashidi, *Nanotechnology* 19 (2008) 315701.