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Influence of coordination groups on the catalytic performances of organo-titanium compounds for disproportionation of methyl phenyl carbonate to synthesize diphenyl carbonate

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Graphical abstract



Highlights

- Electron effect and steric hindrance of the coordination group together affected active Ti center and thereby influenced the catalytic performance.
- Ti(O-*i*C₃H₇)₄ displayed excellent catalytic performance compared to other catalysts reported.
- Suitable steric hindrance and electron effect for the coordination group played important role for outstanding catalytic performance.
- Influence of the electron effect was more important than that of the steric hindrance.
- This work offered an attractive catalyst candidate towards efficient and green processes for MPC disproportionation.

Abstract: The disproportionation of methyl phenyl carbonate (MPC) to synthesize diphenyl carbonate (DPC) catalyzed by organo-titanium compounds with different coordination groups was systematically investigated. The results of the molecular structure analysis, the catalytic performance evaluation and the chemical computational studies revealed that both the electron effect and steric hindrance of the coordination groups together affected the active Ti center and therefore influenced the catalytic performance of the catalysts. The influence of the electron effect was more important than the steric hindrance. The catalytic activity is in the order of $Ti(O-iC_3H_7)_4 > Ti(OC_6H_5)_4 > Ti(OC_4H_9)_4 > TiO(OOCCH_3)_2 > TiO(acac)_2 > Cp_2TiCl_2$ and Ti(O-*i*C₃H₇)₄ exhibited the best catalytic performance, due to its appropriate steric hindrance and electron effect for the coordination group. Under the optimum condition (n(Cat.)/n(MPC)=0.04, reacted at 180 °C for 3 h), the MPC conversion of 90.4% and DPC selectivity of 99.6% were attained, respectively, which are comparable to those of other catalysts reported. Moreover, the catalyst is low cost, non-toxic and easily obtained by readily commercial-available purchase, and this catalytic system is also easy operation and convenient-controllable, indicating that it is conducive to future industrial application. In addition, a possible reaction

mechanism catalyzed by the organo-titanium compounds with Lewis acid was also proposed for the process.

Keywords: methyl phenyl carbonate; diphenyl carbonate; disproportionaton; organo-titanium compounds; steric hindrance and electron effect

1. Introduction

Polycarbonates (PC), as one of the most useful engineering thermoplastics with high transparency, good thermal resistance and mechanical property, was widely used for the synthesis of automobiles, office equipments, medical devices and construction glazing, ect [1, 2]. Diphenyl carbonate (DPC), an important and green chemical intermediate, was frequently employed as the key raw material for the non-phosgene production of PC by a melt polymerization process, and was also utilized in the synthesis of many organic compounds and polymer materials [3-7]. Nowadays, the transesterification of dimethyl carbonate (DMC) and phenol was viewed as one of the most promising routes to synthesize DPC without using phosgene. This route was a two-step process consisting of the transesterification of phenol and DMC into methyl phenyl carbonate (MPC) (Scheme 1, Eq. (1)), followed by the further transesterification reaction of phenol and MPC (Scheme 1, Eq. (2)) or the disproportionation of MPC to DPC (Scheme 1, Eq. (3)) [8, 9]. The equilibrium constants K₂ (1.2×10⁻⁵, 25 °C) and K₃ (0.19, 25 °C) in the second step showed that DPC was mainly generated by the disproportionation of MPC rather than the further transesterification between MPC and phenol [10, 11]. Clearly, the first step was the rate-controlling step, since the equilibrium constant K₁ (6.3×10^{-5} , 25 °C) was much smaller than K_3 , even at elevated temperatures. Thus, previous studies have been mostly focused on the first-step transesterification reaction of phenol and DMC. And the reactivities of the catalysts were also based on the calculation of the total yield of MPC and DPC [12-17]. However, little attention has been paid to the

disproportionation of MPC relative to the first-step transesterification. In fact, MPC must undergo the further disproportionation to generate DPC [18, 19].

unfavorable thermodynamic To avoid the balance limitation on the transesterification reaction, as a result of the K₁ smaller than K₃, it could be divided into two reaction processes, namely including the first-step transesterification reaction and the second independent disproportionation reaction, which was more conducive to improve the yield of the target product DPC, the conversion of raw materials and the intermediate MPC [18]. Furthermore, it was also found that the catalysts were suitable for the first-step transesterification reaction, whereas they did not exhibit good catalytic performance for this disproportionation reaction [19]. Therefore, the exhaustive and intensive study concentrated on the disproportionation of MPC was also very important.

Nevertheless, up to now, the research on MPC disproportionation is rarely reported, and only the catalytic potentials of organo-tin compounds [20], metal based catalysts like PbO [21], MoO₃/SiO₂ [22] and PbO-ZrO₂ [23] have been preliminarily investigated by our research group. The results show that although organo-tin compounds are highly active, it is well known that these compounds are inconvenient for industrial application, due to their high cost, toxicity and environmental contamination. Moreover, metal based catalysts also seem to be unfavorable on the economic feasibility of future large-scale production, because of their lower catalytic activities. Thus, developing highly efficient, economical and environmentally benign sustainable catalytic system and getting insight into the mechanism for this process is still in a great necessity. On the other hand, titanium esters $(Ti(OC_6H_5)_4, Ti(OC_4H_9)_4,$ Ti(O-iC₃H₇)₄, ect.) [24], titanocene complexes (Cp₂TiCl₂) [25], titanium oxide acetylacetonate (TiO(acac)₂) [26] and titanyl acetate (TiO(OOCCH₃)₂) [27] are typical samples of Lewis acids, and they are frequently employed as catalysts for the esterification/transesterification reaction, owning to their much lower price and facile commercial-available purchase. These catalysts are active in the first-step transesterification, however, they have not been used as catalysts for MPC

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disproportionation so far. The MPC disproportionation is a nucleophilic substitution reaction, and it is in essence the Lewis acid catalysis process because Brönsted acid easily results in the decarboxylation of MPC into by-product anisole [18-23]. As our continuous work for exploiting broader kinds of attractive catalysts on the catalytic reaction, it would be quite intriguing to compare the catalytic behaviors of these titanium compounds in terms of their Lewis acid property regarding the Ti center connected to the different coordination groups.

In the present work, organo-titanium compounds with different coordination groups are conducted for MPC disproportionation, and the relationship between the steric hindrance and the electron effect of the coordination groups on their catalytic properties of the organo-titanium compounds are systematically investigated. Also the interactions of the respective Lewis acid-base complex intermediates for organo-titanium compounds are theoretically explored by chemical computational studies. Meanwhile, a possible reaction mechanism catalyzed by organo-titanium compounds is also discussed for the disproportionation.

2. Experimental

2.1. Materials

Titanium oxide acetylacetonate (TiO(acac)₂, 99.6%), tetraphenyl titanate (Ti(OC₆H₅)₄, 99.6%), tetrabutyl titanate (Ti(OC₄H₉)₄, \geq 98%), titanium isopropoxide (Ti(O-*i*C₃H₇)₄, \geq 98%) were purchased from Alfa Aesar Chemical Reagent Company. Titanocene dichloride (Cp₂TiCl₂, 99.7%) was provided from Hubei Huabang Chemical Reagent Company of China. Titanyl acetate (TiO(OOCCH₃)₂) was synthesized according to the literature [27]. Cp₂TiCl₂, TiO(acac)₂, Ti(OC₆H₅)₄ and TiO(OOCCH₃)₂ were solid powder. Ti(OC₄H₉)₄ and Ti(O-*i*C₃H₇)₄ were colorless transparent liquid. Before the reaction, Cp₂TiCl₂, TiO(acac)₂, Ti(OC₆H₅)₄ and TiO(OOCCH₃)₂ were dried in a vacuum oven at 70 °C, while Ti(OC₄H₉)₄ and Ti(O-*i*C₃H₇)₄ were dried at 20 °C in the presence of 4A molecular sieves.

2.2. Catalytic performance tests

MPC was synthesized and purified in the laboratory, and its purity was 99.8% determined by high performance liquid chromatography. The synthesis procedure was as follows: due to the small thermodynamic equilibrium constant of MPC disproportionation reaction, MPC could be synthesized beneficially by the reversible disproportionation of DMC and DPC. Subsequently, the separation of high purity MPC was carried out by the pressure reduction distillation and rectification. Finally, the quantitatively analysis of MPC was performed by the high performance liquid chromatography.

The liquid-phase disproportionation reaction of MPC was carried out in a 100 mL three necked round bottom flask fitted with a fractionation column connected to a liquid dividing head. Typically, the reactor was gently purged with nitrogen to evacuate the air, and then 150 mmol MPC and an appropriate amount of catalyst were added into the reactor under nitrogen atmosphere. The reactor was gradually heated to the desired temperature in an oil bath, and it was subsequently maintained at the desired temperature with a constant stirring rate. During the reaction, DMC was continuously distilled out by the liquid dividing head attached to a receiver flask. After the reaction, the reactor was slowly cooled to room temperature (20 °C).

After the reaction, the reaction mixture and the distilled liquid are respectively detected by GC-MS instrument with a HP-5 capillary chromatography packed column (30 m \times 250 µm \times 0.25 um) on a HP-6890/5973 system. The reaction mixture is mainly composed of the raw material MPC and the product DPC, and there is also a tiny amount of by-product anisole. The distilled liquid is DMC without any by-product. The products were quantitatively analyzed by GC system (Agilent Technologies 7820A) with a flame ionization detector (HP/DB, capillary chromatography packed column) and a DB–35 capillary column (30 m \times 320 µm \times 0.25 µm) using the correction factor normalization method.

The conversion of MPC, the yield and selectivity of DPC were calculated as follows:

$$Conv / \% = \frac{n_o - n_{MPC}}{n_o} \times 100\%$$

$$Y / \% = \frac{n_{DPC}}{n_o} \times 100\%$$
$$Sel / \% = \frac{Y\%}{Conv\%} \times 100\%$$

As to the calculation, *Conv* was denoted as the conversion of MPC, %; *n*₀ and *n*_{MPC} were the mole substance amounts of MPC before and after the reaction, respectively; *Y* was denoted as the yield of DPC, %; *n*_{DPC} was the mole substance amount of DPC; *Sel* was denoted as the selectivity of DPC, %.

2.3. Theoretical studies

To understand the catalyzing behavior of these titanium compounds, their geometrical structures were fully optimized without any restriction. The three-parameter fit to the exchange-correlation potential suggested by Beck in conjunction with the correlation functional suggested by Lee, Yang and Parr (B3LYP) was adopted with the basis set of 6-31++G (d, p) level [28]. Frequency calculations were carried out at the optimized structures to confirm a real local minimum (no imaginary frequency). The gaps between the frontier orbitals, i.e., the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO), were correlated to the catalyzing ability. All calculations were performed with Gaussian 09 programs package [29].

3. Results and discussion

3.1. Effect of the coordination groups on the disproportionate performances of the organo-titanium compounds

Organo-titanium compounds with different coordination groups are used to catalyze the disproportionation of MPC, and the effect of the coordination groups on their catalytic performances are investigated and the results are summarized in Table 1. The catalyst dosage is on the basis of the active Ti center, and the mole ratio of Ti to MPC is 0.04. As can be seen in Table 1, evidently, the disproportionation reaction could not proceed without catalyst. Organo-titanium compounds with different coordination groups have notable catalytic activities for the disproportionation, and the selectivities of DPC are more than 96.0%. Among them, titanium esters exhibit higher catalytic activities, giving the MPC conversion of more than 86.2%. For these titanium compounds tested, the sequence of the catalytic activities is observed as follows: $Ti(O-iC_3H_7)_4 > Ti(OC_6H_5)_4 > Ti(OC_4H_9)_4 > TiO(OOCCH_3)_2 > TiO(acac)_2 > Cp_2TiCl_2$, which may be resulted from the influence of both the steric hindrance and the electron effect of the coordinating groups associated with the active Ti center [30].

Organo-titanium is as Lewis acid and the Ti is active center. The electron effect of the coordination group influences the electron cloud density of the Ti, while the steric hindrance of the coordination group influences the difficulty level of Ti contacting with the reactant molecules [31-34]. Specifically, they together affect the catalytic activity of the Ti. Cp₂TiCl₂ displays sandwich molecular structure [25], and its steric hindrance is much larger than other organo-titanium compounds, increasing the difficulty of Ti contacting with the oxygen of the carbonyl group of MPC. Therefore, its reactivity is the lowest, and only 31.4% MPC conversion is obtained. Likewise, the steric hindrance of Ti(O-*i*C₃H₇)₄ is smaller than those of Ti(OC₆H₅)₄ and Ti(OC₄H₉)₄, and thus the reactivity of Ti(O-*i*C₃H₇)₄ is higher in comparison with Ti(OC₆H₅)₄ and Ti(OC₄H₉)₄.

As to Ti(OC₆H₅)₄ and Ti(OC₄H₉)₄, the corresponding coordination groups of the Ti are phenoxyl and butoxyl. As a consequence of the conjugated effect of benzene ring, the electron withdrawing ability of phenoxyl group is stronger than that of butoxyl group, and therefore the Lewis acidity of the Ti in Ti(OC₆H₅)₄ is higher than that in Ti(OC₄H₉)₄. Although the steric hindered space of the phenoxyl group is larger than that of butoxyl group, the reactivity of Ti(OC₆H₅)₄ is still higher than Ti(OC₄H₉)₄, suggesting that the influence of the electron withdrawing effect is larger than that of the steric hindrance. Furthermore, the high Lewis acidity of Ti(OC₆H₅)₄ makes the conversion of MPC close to that of Ti(O-*i*C₃H₇)₄. Nevertheless, the high Lewis acidity of Ti(OC₆H₅)₄ also results in the decarboxylation of MPC to produce anisole [20, 35], thereby causing the selectivity of DPC lower than those over $Ti(O-iC_3H_7)_4$ and $Ti(OC_4H_9)_4$.

 $TiO(OOCCH_3)_2$ usually appears as the dimmers and displays six coordination octahedral structure [27]. Its steric hindrance is significantly greater than that of $Ti(OC_4H_9)_4$. Accordingly, the reactivity of $TiO(OOCCH_3)_2$ is lower than $Ti(OC_4H_9)_4$.

The steric hindrance of $TiO(OOCCH_3)_2$ is remarkably bigger compared to that of $TiO(acac)_2$, but from the point of view of the electron effect, the electron withdrawing ability of acetoxy group is stronger than that of acetylacetonate group, making the Lewis acidity of $TiO(OOCCH_3)_2$ higher than that of $TiO(acac)_2$, and hence the catalytic activity of $TiO(OOCCH_3)_2$ is higher than that of $TiO(acac)_2$. The results also show that the influence of the electron effect is greater than that of the steric hindrance.

3.2. Theoretical studies

The disproportionation of MPC is Lewis acid catalysis process. As shown in Fig. 1, according to the literatures [36, 37], the Lewis acid-base complex intermediate is formed by the interaction/coordination of MPC with the metal Ti center via the oxygen of the carbonyl group, and then this interaction activates MPC to undergo subsequent nucleophilic attack. In view of the orbital interaction of the Lewis acid-base complex intermediate, it is thought as a result of an overlap between the lower unoccupied molecular orbital (LUMO) of the Lewis acid Ti center and the higher occupied molecular orbital (HOMO) of the oxygen Lewis base of the carbonyl group, as shown in Fig. 2. If the energy gaps between HOMO_{carbonyl}–LUMO_{complex} of respective species are quite close, the Lewis acid-base interactions will be more effective for readily activating MPC to undergo subsequent nucleophilic attack. Therefore, the chemical computational studies are carried out, and the results are listed in Table 2.

According to the energies calculated in Table 2, $TiO(acac)_2$ shows the lowest orbital energy, meaning that the strongest Lewis acid-base interaction occurs between $TiO(acac)_2$ and the carbonyl group of MPC. And the interaction intensity of the

respective Lewis acid-base complex intermediates for organo-titanium compounds is in the order of TiO(acac)₂ > TiO(OOCCH₃)₂ > Cp₂TiCl₂ > Ti(OC₆H₅)₄ > Ti(OC₄H₉)₄ > Ti(O-*i*C₃H₇)₄, which is different from the order of their catalytic activities, further suggesting that the influence of the electron effect is not the only factor, and other features like the steric hindrance also play very important role on this activation process. Considering the structural similarity of Ti(OC₆H₅)₄, Ti(OC₄H₉)₄ and Ti(O-*i*C₃H₇)₄, Ti(OC₆H₅)₄ with the larger steric hindrance and the lower orbital energy presents higher catalytic activity, indicating that the influence of the electron effect is greater than that of the steric hindrance, which is in accordance with the above analysis.

In general terms, the steric hindrance and the electron effect of the coordination group together affect the active Ti center and therefore influence the catalytic activity. The smaller the steric hindrance of the coordination group is, the higher the reactivity of organo-titanium compound is. The stronger the electron withdrawing group is, the stronger the Lewis acidity of the Ti is, and thereby higher catalytic activity is obtained. Nevertheless, higher Lewis acidity can also results in MPC decomposition to decarboxylate into by-product anisole [38]. Among these titanium compounds explored, Ti(O-iC₃H₇)₄ exhibits the best catalytic performance, the conversion of MPC reaches up to 90.4%, and the yield and selectivity of DPC are 90.0% and 99.6%, respectively, which are comparable to those of organo-tin compounds, metal oxides, MoO₃/SiO₂, and PbO-ZrO₂, since BuSnO(OH) showed the best catalytic performances with the MPC conversion of 89.7% and DPC selectivity of 99.3% [20]. Moreover, Ti(O-*i*C₃H₇)₄ is cheap, innocuous and commercially available. Even though the TOF of 10 h⁻¹ for Ti(O-*i*C₃H₇)₄ in the reaction system is lower than those catalyzed by organo-tin compounds (TOF: 18 h⁻¹) and mixed metal oxides (TOF: 54 h⁻¹), it is noteworthy that the catalyst is not only appropriate for the first-step transesterification reaction, but also can efficiently catalyze the second-step disproportionation reaction. As a result, when the first-step transesterification reaction is finished, the catalyst does not be separated or purified from the reaction mixture and may be directly performed for the subsequent second-step disproportionation reaction by adjusting the reaction

conditions, which can simplify the operation process and improve the reaction efficiency in practical production. These advantages suggest its good potential for industrial application in the future. On the whole, as has been already stated, $Ti(O-iC_3H_7)_4$ is a suitable Lewis acid catalyst for the disproportionation, and in order to better understand the catalytic reaction as well as realize the industrial application preliminary explored, the effect of reaction time, reaction temperature as well as the catalyst amount is further investigated for $Ti(O-iC_3H_7)_4$.

3.3. Effect of the reaction time

Fig. 3 shows the effect of reaction time on the disproportionation of MPC. The conversion of MPC increases sharply with reaction time increase before 3 h, and the selectivity of DPC slightly changes. After 3 h, MPC conversion of 90.4% is attained, and the selectivity of DPC is 99.6%. Continuing to increase the reaction time, the conversion of MPC and the selectivity of DPC keep almost unchanged thereafter. The result indicates that the disproportionation nearly achieves equilibrium at 3 h. Hence, the optimum reaction time is 3 h. Besides, the reaction operation is simple, mild and controllable, which is conducive to the industrial application in future.

3.4. Effect of the reaction temperature

Thermodynamic calculation shows that the disproportionation reaction temperature controlled in the range of 160 to 200 °C is favorable [18], thus the influence of temperature on the disproportionation is studied and the results are presented in Fig. 4. The conversion of MPC increases quickly from 76.5% to 89.3% when the reaction temperature is raised from 150 to 180 °C, and the selectivity of DPC slightly changes. Nevertheless, the selectivity of DPC begins to decrease as the temperature further increases to 200 °C, which can be attributed to the decarboxylation decomposition of MPC into anisole at the higher temperatures [39]. The results suggest that a higher reaction temperature not only favors the production of DPC and in the mean time, but also raises the risk of MPC decomposition. Therefore, the optimum reaction temperature is 180 °C, and the conversion of MPC and the selectivity of DPC is

89.3% and 99.4%, respectively.

3.5. Effect of the catalyst amount

Fig. 5 shows the effect of catalyst amount on the disproportionation of MPC, and the catalyst amount is based on the calculation of $Ti(O-iC_3H_7)_4$ to MPC mole ratio. As expected, the conversion of MPC gradually increases as the mole ratio of $Ti(O-iC_3H_7)_4$ to MPC increases, and the selectivity of DPC remains almost unchanged. When the mole ratio is increased to 0.04, the conversion of MPC reaches to 89.5%, and the selectivity of DPC is 99.6%. With further increase the mole ratio to 0.06, the conversion of MPC slightly increases, whereas the selectivity of DPC distinctly decreases. The reason may be that $Ti(O-iC_3H_7)_4$ is Lewis acid, and the acid amount of the reaction system increases with the increase catalyst dosage. As a result, anisole is easily produced, since higher acid amount can result in MPC decarboxylation [40]. Therefore, the appropriate mole ratio for the present system is 0.04.

3.6. Possible mechanism for the catalytic reaction

In general, Ti(O-*i*C₃H₇)₄ as Lewis acid is a typical kind of soluble transition metal coordination complexes catalyst in organic reaction, and the Ti is the active site. It is worth noting that the disproportionation of MPC is a nucleophilic substitution reaction process, and MPC is the only reaction reactant. Hence, the carbonyl group must be activated firstly, and then the subsequent reaction takes place [20-22, 24, 25, 30, 41]. Moreover, FTIR-online detection technique is used to monitor the reaction process (see Supplementary material). In view of these, a possible reaction mechanism for the disproportionation catalyzed by Ti(O-*i*C₃H₇)₄ is proposed in Scheme 2. The Ti firstly activates the oxygen of the carbonyl group to produce the chelate, making the carbonyl carbon even electropositive. Subsequently, it attacks another molecular MPC to form four atoms transition state Ti complexes, and then undergoes the nucleophilic substitution to generate DPC and DMC, completing the catalytic cycle. If the final product DMC continuously is distilled off, the reaction can be continuously proceeded towards DPC.

4. Conclusions

The catalytic performances of organo-titanium compounds with various coordination groups for MPC disproportionation were investigated. The results showed that the steric hindrance and electron effect of the coordination groups together influenced their catalytic performances. The influence of the electron effect was greater than that of the steric hindrance. The smaller the steric hindrance of the coordination group was, the higher the reactivity of organo-titanium was. Besides, the stronger the electron withdrawing effect of the coordination groups was, the stronger the Lewis acidity of the Ti was, and the higher the catalytic activity was. Nevertheless, excessive strong Lewis acidity easily resulted in the decarboxylation of MPC to anisole. Among the titanium compounds screened, Ti(O-iC3H7)4 showed the best catalytic performance for its suitable steric hindrance and electron effect for the coordination groups. Under the optimal condition, with 0.04 of n(Cat.)/n(MPC), 180 °C of reaction temperature and 3 h of reaction time, MPC conversion of 90.4% and DPC selectivity of 99.6% were achieved. Furthermore, the catalytic system was easily handled and convenient, and especially the catalyst with relatively low price and commercially available purchase was beneficial to industrial purposes in the near future. Thus, this work offered an attractive alternative candidate of catalysts towards efficient and green processes for transforming MPC disproportionation into DPC. In addition, the possible reaction mechanism over Lewis acid titanium compounds was proposed for the disproportionation. The active Ti firstly coordinated the oxygen of the carbonyl group to form transition state Ti complexes, and then undergo the nucleophilic substitution attack to generate DPC, completing the catalytic reaction.

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Lewis acid-base complex

Fig. 1. Schematic illustration of the oxygen activation of the carbonyl group via the Lewis acid-base interactions.



Fig. 2. Two different orbital energies of the Lewis acid-base interactions, and (A) is more efficient due to the lower orbital energies.



Fig. 3. Effect of reaction time on the disproportionation of MPC.

Reaction conditions: 180 °C, n(Cat.)/n(MPC) 0.04, catalyst Ti(O-*i*C₃H₇)₄, MPC 150 mmol.



Fig. 4. Effect of reaction temperature on the disproportionation of MPC.

Reaction conditions: 3 h, n(Cat.)/n(MPC) 0.04, catalyst Ti(O-iC₃H₇)₄, MPC 150 mmol.



Fig. 5. Effect of catalyst amount on the disproportionation of MPC. Reaction conditions: 180 °C, 3 h, catalyst $Ti(O-iC_3H_7)_4$, MPC 150 mmol.



Scheme 1. Transesterification reaction of DMC and phenol to produce DPC.



Scheme 2. Possible reaction mechanism for MPC disproportionation.

Catalysts	MPC	Yields (%)		DPC
	conversion (%)	DPC	Anisole	selectivity (%)
_	trace	trace	0	trace
Cp ₂ TiCl ₂	31.4	30.3	1.1	96.5
TiO(acac) ₂	69.2	68.3	0.9	98.7
TiO(OOCCH ₃) ₂	71.1	69.5	1.6	97.7
Ti(OC ₄ H ₉) ₄	86.2	85.6	0.6	99.3
Ti(OC ₆ H ₅) ₄	89.1	87.8	1.3	98.5
$Ti(O-iC_3H_7)_4$	90.4	90.0	0.4	99.6

Table 1 Catalytic performance of organo-titanium compounds for MPC disproportionation

Reaction condition: 180 °C, 3 h, MPC 150 mmol, n(Cat.)/n(MPC) 0.04.

Table 2 Frontiers molecular orbitals of the catalysts and MPC

Catalysts	LUMO _{complex} (eV)	$\Delta E \text{ of HOMO}_{carbonyl}$ -LUMO _{complex} ^a (eV)
TiO(acac) ₂	-3.83	3.21
TiO(OOCCH ₃) ₂	-3.22	3.82
Cp ₂ TiCl ₂	-3.04	4.00
Ti(OC ₆ H ₅) ₄	-2.02	5.02
Ti(OC ₄ H ₉) ₄	-1.01	6.03
$Ti(O-iC_3H_7)_4$	-0.94	6.10

^a Modular measure of HOMO–LUMO involves the HOMO of MPC (HOMO_{carbonyl}) and the LUMO of the related catalyst (LUMO_{complex}), and the orbital energy of MPC is -7.04 eV.