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Organotin-oxomolybdate coordination polymer as catalyst for synthesis of unsymmetrical organic carbonates

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Efficient and greener synthesis of unsymmetrical organic carbonates is of great importance. In this work, two organotin-oxometalates, Bu_2SnMoO_4 and $(Bu_3Sn)_2MoO_4$, were prepared and their catalytic performance for the transesterification of diethyl carbonate (DEC) with alcohols to synthesize unsymmetrical organic carbonates was studied. It was found that $(Bu_3Sn)_2MoO_4$ was very active and selective for the transesterification of DEC and various alcohols, including alkyl, cyclic, and aryl alcohols due to the synergetic effect between the groups of $[MoO_4]^{2-}$ and $[Bu_3Sn]^+$ in the catalyst. The yields of the corresponding carbonates could reach 98% at the suitable conditions. The catalyst was reused five times and the activity and selectivity were not changed. We believe that the highly efficient, versatile, greener, inexpensive, selective and stable catalyst has great potential applications in the synthesis of various unsymmetrical organic carbonates from DEC and alcohols.

Introduction

Dialkyl organic carbonates are very attractive from a green chemistry point of view.¹ They have been used as intermediates for the synthesis of pharmaceuticals and fine chemicals,² as excellent polar aprotic solvents,³ as monomers for organic glass, synthetic lubricants and plasticizers,⁴ as octane enhancers for gasoline,⁵ in agriculture to produce herbicides, acaricides, fungicides and seed disinfectants.⁶

Conventional synthetic methods for organic carbonates use toxic and harmful chemicals such as phosgene, pyridine and carbon monoxide.⁷ To avoid the use of the toxic reagents, in recent years, symmetrical organic carbonates, especially dimethyl carbonate (DMC) and diethyl carbonate (DEC), have been synthesized by CO₂, epoxides and alcohols,^{8a-8e} or synthesized directly from CO₂ and alcohols.^{8f}

Compared to symmetrical organic carbonates, unsymmetrical organic carbonates are more useful molecules than the symmetrical ones, but the synthetic routes are more complex. Several methods have been developed for the production of unsymmetrical organic carbonates. For example, electrochemical synthesis of organic carbonates from CO_2 and alcohols has been conducted in ionic liquids.⁹ Some unsymmetrical organic carbonates have been produced by the coupling of alcohols, CO_2 and alkyl halides in the presence of Cs_2CO_3 .¹⁰ Furthermore,

carbonates have been synthesized from primary or secondary alcohols and CO₂ *via* unstable methanesulfonyl carbonates.¹¹ Recently, Chi and co-workers reported the synthesis of organic carbonates *via* alkylation of metal carbonate with various alkyl halides and sulfonates in ionic liquids.¹²

The unsymmetrical organic carbonates can also be prepared by transesterification of DEC with various alcohols. Different heterogeneous catalysts, including MCM-41-TBD,¹³ Mg/La metal oxide,¹⁴ CsF/ α -Al₂O₃,¹⁵ nano-crystalline MgO¹⁶ and metal–organic frameworks¹⁷ have been used for the reactions. However, development of highly efficient synthetic routes for the production of unsymmetrical organic carbonates is an interesting topic.

Recently, tri-*n*-butyltin derivatives have been reported by Fischer and co-workers.¹⁸ These compounds, having the general formula $[(R_3Sn)_2MO_4]$ [R = Me, Et, *n*-Pr, *n*-Bu and phenyl (Ph); M = Mo and W], are formed through the coordination of the tetrahedral $[MO_4]^{2-}$ subunits and $[R_3Sn]^+$ as the linking spacers (Scheme 1). These compounds are interesting candidates as catalysts or catalyst precursors and have been used in some oxidation reactions, such as epoxidation of olefins,¹⁹ sulfoxidation,²⁰ *N*-oxidation of primary aromatic amines,²¹ *etc.* It is interesting to extend the application of these compounds as catalysts for more chemical reactions.

In this work, we prepared two organotin-oxometalates, Bu_2SnMoO_4 and $(Bu_3Sn)_2MoO_4$, and their catalytic performance for the transesterification of DEC with various alcohols to synthesize unsymmetrical organic carbonates was studied. It was found that the organotin-oxometalates, especially $(Bu_3Sn)_2MoO_4$, are very active, selective and stable for the

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Scheme 1 Representation of the proposed structure of $(R_3Sn)_2MO_4$.

reactions. To the best of our knowledge, this is the first application of organotin-oxometalates to catalyze the transesterification of alcohols with dialkyl organic carbonates.

Results and discussion

Characterization of the catalysts. The organotinoxometalates, Bu₂SnMoO₄ and $(Bu_3Sn)_2MoO_4$, were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and thermogravimetric (TG) techniques. The powder XRD patterns are presented in Fig. 1. The XRD pattern of the (Bu₃Sn)₂MoO₄ was in good agreement with that reported by other authors²¹ The patterns of the Bu₂SnMoO₄ and (Bu₃Sn)₂MoO₄ were quite different, suggesting that the tin-bound group exerts a considerable structure directing effect. Meanwhile, the powder XRD patterns of Bu₂SnMoO₄ and (Bu₃Sn)₂MoO₄ showed characteristic peaks of MoO₄ in the range of 2θ (22), which are similar to the data reported in the literature.²¹ FT-IR spectra of Bu₂SnMoO₄ and (Bu₃Sn)₂MoO₄ showed all characteristic bands of organic and metal organic functionalities present in the coordination polymers. The strong band at 810 cm⁻¹ in the FT-IR spectra of the two compounds (Fig. 2) was assigned to the asymmetric stretch of the $[MoO_4]^{2-1}$ oxoanion and this is in agreement with published result.²⁰



Fig. 1 Powder X-ray diffraction pattern for $(Bu_3Sn)_2MoO_4$ (a) and Bu_3SnMoO_4 (b).



Fig. 2 FT-IR spectra for $(Bu_3Sn)_2MoO_4$ (a) and Bu_2SnMoO_4 (b).

The observed strong peaks at about 1460 cm⁻¹ and 2900 cm⁻¹ should be assigned to the stretch of *n*-butyl (*n*-Bu) The TG thermograms of the two compounds (Fig. 3) indicated that they had very good thermal stability. The weights of the Bu₂SnMoO₄ and (Bu₃Sn)₂MoO₄ remained almost constant up to 240 °C and 250 °C, respectively. The decomposition of the coordination polymers occurred at about 240 °C and 250 °C, respectively, which is much higher than the temperature used in the reaction. The weight loss which occurred at about 650 °C resulted from the decomposition of oxides of Sn or Mo.

Catalytic performance of different catalysts. The activity and selectivity of various catalysts were tested for the transesterification of 1-octanol and DEC, and the results are given in Table 1. In the absence of the catalyst, the desired unsymmetrical carbonate was not formed (Table 1, entry 1). Similarly, the reaction did not occur when only the precursors of the organotinoxometalates, such as Na₂MoO₄·2H₂O, BuSnCl₃, Bu₂SnCl₂, Bu₃SnCl, were used as the catalysts (Table 1, entries 2–5). The $(NH_4)_6Mo_7O_{24}$ ·4H₂O alone just gave a moderate yield (Table 1, entry 6). To our delight, when Na₂MoO₄·2H₂O and Bu₃SnCl were used at the same time, the reaction took place with about 30% yield of the desired product (Table 1, entry 7). The insoluble nature of Na2MoO4·2H2O in the reaction system resulted in slow formation rate of (Bu₃Sn)₂MoO₄. Therefore, the yield of the desired product catalyzed by physical mixture of Na₂MoO₄·2H₂O and Bu₃SnCl was lower than that catalyzed by (Bu₃Sn)₂MoO₄. On the base of this finding, we synthesized two organotinoxometalates (Bu₂SnMoO₄ and (Bu₃Sn)₂MoO₄) as the catalysts for the transesterification reaction. Surprisingly, the reaction proceeded with much higher yield (Table 1, entries 8 and 9) and

Table 1 Reaction of 1-octanol and DEC catalyzed by different catalysts"

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Entry	Catalyst	Yield(%) ^b	Selectivity(%)			
1	None	0				
2	Na ₂ MoO ₄ ·2H ₂ O	0	_			
3	BuSnCl ₃	0	_			
4	Bu ₂ SnCl ₂	0	_			
5	Bu ₃ SnCl	0	_			
6	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	47	97			
7 ^d	$Na_2MoO_4 \cdot 2H_2O + Bu_3SnCl$	30	97			
8	Bu ₂ SnMoO ₄	80	99			
9	$(Bu_3Sn)_2MoO_4$	98	99			

^{*a*} Typical reaction conditions: a flask of 10 ml, 33 mmol DEC, 2 mmol 1-octanol, 15 mg catalyst, reaction temperature 130 °C, reaction time 2 h. ^{*b*} The yields were determined by GC. ^{*c*} The by-product was mainly octanoyl ethyl ether, corresponding di-ether and product of alcohol oxidation. ^{*d*} 5 mg Na₂MoO₄·2H₂O and 13 mg Bu₃ClSn were used, which could form 15 mg (Bu₃Sn)₂MoO₄.



 $\label{eq:Fig.3} Fig. \ 3 \quad Thermogram \ of \ (Bu_3Sn)_2MoO_4 \ (a) \ and \ Bu_2SnMoO_4 \ (b).$

the selectivity to the corresponding unsymmetrical carbonate was 99% in the presence of Bu_2SnMoO_4 or $(Bu_3Sn)_2MoO_4$. In addition, $(Bu_3Sn)_2MoO_4$ had the best catalytic activity (Table 1, entry 9). This increased activity is likely to be due to the synergetic effect between the groups of $[MoO_4]^{2-}$ and $[Bu_3Sn]^+$, which existed in the organotin-oxometalate. Therefore, $(Bu_3Sn)_2MoO_4$ was used as the catalyst for further study.

Table 2 Effect of reaction temperature on the reaction of 1-octanol and DEC^a

Entry	T∕°C	Yield(%) ^b	Selectivity(%) ^c
1	100	0	_
2	110	17	99
3	120	51	99
4	130	98	99

^{*a*} Typical reaction conditions: a flask of 10 ml, 33 mmol DEC, 2 mmol 1-octanol, 15 mg (Bu₃Sn)₂MoO₄, reaction time 2 h. ^{*b*} The yields were determined by GC. ^{*c*} The byproduct was mainly octanoyl ethyl ether, corresponding di-ether and product of the alcohol oxidation.

The effects of catalyst amount and temperature on the reaction. The influence of the amount of $(Bu_3Sn)_2MoO_4$ on the transesterification of 1-octanol with DEC was investigated under the identical reaction conditions (Fig. 4). The selectivity to the corresponding unsymmetrical organic carbonate was about 99% as the amount of the catalyst was in the range of 5 to 20 mg. The byproducts were mainly octanoyl ethyl ether, corresponding diether and product of the alcohol oxidation. The yield increased with the amount of the catalyst and reached a 98% as the amount of the catalyst was increased up to 15 mg. Therefore, 15 mg of the catalyst would be an appropriate amount at the reaction conditions.



Fig. 4 Effect of catalyst amount on the transesterification of 1-octanol with DEC. Reaction conditions: a flask of 10 ml, 33 mmol DEC, 2 mmol 1-octanol, reaction temperature 130 °C, reaction time 2 h.

Furthermore, we found that the yield of the corresponding unsymmetrical organic carbonate was strongly affected by the reaction temperature using $(Bu_3Sn)_2MoO_4$ as the catalyst. As shown in Table 2, the yield increased with temperature in the range of 100 to 130 °C and a yield of 98% was achieved at 130 °C.

Reactions of DEC with different alcohols. The catalytic performance of $(Bu_3Sn)_2MoO_4$ for the reactions of DEC with various kinds of alcohols including alkyl, cyclic, and aryl alcohols was also examined. $(Bu_3Sn)_2MoO_4$ showed satisfactory activity and selectivity for the transesterification reactions, as can be known from the data in Table 3. The activity of the primary alkyl alcohols was very high and they were all transformed into the corresponding unsymmetrical carbonates with good selectivity (Table 3, entries 1–6). The activity order of alkyl alcohols was primary alcohol > secondary alcohol > tertiary

			$\sim \frac{(Bu_3Sn)_2MoO_4}{130^{\circ}C, t} RO^{\circ}$	o + EtOH	
Entry	Alcohol	Product	Tir	ne(h) Yield(%)) ^b Selectivity(%) ^c
1	√ → ОН	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	2	99	99
2	√()_5 ОН	$\sim \gamma_{5}^{\circ}$	2	98	99
3	√()_0H		2 2	98	98
4	∽(турон	$\sim \sim $	2	97	99
5	√турон		2	98	98
6	~()_он		2	97	98
7		он ` ~~~~	°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°	98	98
8	ОН	` ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°	0	_
9	Стон	L L	4	94	97
10	Стон		2	98	98
11	ОН	Q.i.	8	96	97
12	С, тон		*	81	98
13	СООН		8	90	95
14	Стон			93	97
15	OH		*	79	90

Table 3 Synthesis of unsymmetrical organic carbonates from DEC and various alcohols catalyzed by (Bu₃Sn)₂MoO₄^a

^{*a*} Typical reaction conditions: a flask of 10 ml, 33 mmol DEC, 2 mmol alcohol, 15 mg $(Bu_3Sn)_2MoO_4$, reaction temperature 130 °C. ^{*b*} The yields were determined by GC. ^{*c*} The by-product was mainly corresponding ether, di-ether and product of the alcohol oxidation.

alcohol (Table 3, entries 3, 7 and 8), which could result mainly from steric hindrance of the three types of alcohols and tertiary alcohols have the largest steric hindrance. The aryl alcohols (Table 3, entries 13–15) had lower activity than the alkyl ones because the π electron of the benzene ring could be combined with the activity center of the catalyst, which reduced the interaction chance of the reactants and the catalyst, and this effect of π electron also existed in the alkyl alcohols (Table 3, entries 9 and 10). The aryl alcohols also showed the same activity order of primary alcohol > secondary alcohol (Table 3, entries 14 and 15). For the cyclic alcohols (Table 3, entries 11 and 12), the lower activity was due to the steric hindrance of the ring.

Reusability of the catalyst. Experiments were also carried out to examine the recyclability of the catalyst using 1-hexanol as the substrate. In each cycle, $(Bu_3Sn)_2MoO_4$ was recovered by distillation at reduced pressure. Then, the catalyst was reused directly for the next run. The yields of the corresponding carbonate for the five repeated runs are shown in Fig. 5. There was no considerable decrease in the yield and selectivity of the corresponding carbonate after five cycles, indicating that the catalyst was very stable.



Fig. 5 Reuse of the catalyst. Reaction conditions: 15 mg $(Bu_3Sn)_2MoO_4$, 2 mmol 1-hexanol, 33 mmol DEC, reaction temperature 130 °C, reaction time 2 h.

Mechanism. A plausible mechanism was proposed based on a typical transesterification process (Scheme 2), where the more nucleophilic reagent displaces the less nucleophilic one or the less volatile compound displaces the more volatile one when both the reagents have similar nucleophilicity. In the present process, the nucleophilic displacement of the ethoxy group by a second molecule of the alcoholic reagent probably leads to the corresponding unsymmetrical carbonate. As shown in Scheme 2, the catalytic cycle may be initiated by activation of an alcohol through hydrogen bonding formed between hydroxyl group and [MoO₄]²⁻ in the catalyst and meanwhile, DEC was activated by the group $[Bu_3Sn]^+$ [(a) in Scheme 2]. Then, the activated alcohol attacked the activated carbonyl group of DEC [(b) in Scheme 2]. Finally, the corresponding unsymmetrical carbonates were formed through an intermediate [(c) in Scheme 2]. From the discussion above, we think that the synergistic effect of [MoO₄]²⁻ and [Bu₃Sn]⁺ existing in the catalyst may be the main reason for the high activity of the catalyst system.



Scheme 2 Plausible mechanism for synthesis of unsymmetrical organic carbonates catalyzed by the $(Bu_3Sn)_2MoO_4$.

Conclusions

 $(Bu_3Sn)_2MoO_4$ is an very efficient catalyst for the synthesis of unsymmetrical organic carbonates through the transesterification of DEC with various alcohols due to the synergetic effect between the groups of $[MoO_4]^2$ and $[Bu_3Sn]^+$ in the catalyst. The yields of the unsymmetrical organic carbonates can be as high as 98%. The activity of alkyl alcohols follows the order primary alcohol > secondary alcohol > tertiary alcohol, which result mainly from the difference of steric hindrance of the alcohols. The aryl alcohols also show the same activity order of primary alcohol > secondary alcohol. The catalyst can be reused at least five times without reducing the activity and selectivity. We believe that the catalyst has great potential applications in the synthesis of various unsymmetrical organic carbonates from DEC and alcohols.

Experimental

Materials

Diethyl carbonate, *n*-Bu₃SnCl, *n*-Bu₂SnCl₂, *n*-BuSnCl₃ were purchased from Alfa Aesar. The alcohols, $Na_2MoO_4 \cdot 2H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, acetone were all analytical grade and purchased from Beijing Chemical Reagents Company. All chemicals were used as received.

Methods

FT-IR spectra were recorded on a spectrometer (Bruker Tensor 27, Germany) and the sample was prepared by the KBr pellet method. XRD measurements were conducted on an X-ray diffractometer (D/MAX-RC, Japan) operated at 40 kV and 200 mA with Cu-K α ($\lambda = 0.154$ nm) radiation. TG analysis was performed on a thermogravimetric analysis system (Netzsch STA 409 PC/PG, Germany) in N₂ atmosphere at a heating rate of 20 °C min⁻¹.

Catalyst synthesis

The catalysts were prepared according to the procedure reported by Fischer and co-workers.¹⁸

Synthesis of [(*n*-Bu₃Sn)₂MoO₄]. *n*-Bu₃SnCl (10 mmol) was dissolved in a solution of water (6 mL) and acetone (27 mL). An aqueous solution of Na₂MoO₄·2H₂O (5 mmol in 8 mL of H₂O) was added dropwise with magnetic stirring to *n*-Bu₃SnCl solution. A white precipitate was formed immediately and stirring was continued for 0.5 h. The precipitate was filtered, washed thoroughly with water and acetone, and dried under vacuum at 80 °C for 12 h. Anal. Found: 38.85% C, 7.45% H. Calcd. for C₂₄H₅₄Sn₂MoO₄ (740.02): 38.95% C, 7.36% H.

Synthesis of [*n*-Bu₂SnMoO₄]. *n*-Bu₂SnCl₂ (5 mmol) was dissolved in a mixture of water (6 mL) and acetone (27 mL). An aqueous solution of Na₂MoO₄·2H₂O (5 mmol in 8 mL of H₂O) was added dropwise to *n*-Bu₂SnCl₂ solution with magnetic stirring. A white precipitate was formed immediately and stirring was continued for 0.5 h. The precipitate was filtered, washed thoroughly with water and acetone, and dried in vacuum at 80 °C for 12 h. Anal. Found: 24.37% C, 4.66% H. Calcd. for C₈H₁₈SnMoO₄ (392.86): 24.46% C, 4.62% H.

Catalytic reaction

In a typical procedure, DEC (33 mmol, 4 mL), alcohol (2 mmol) and catalyst (15 mg) were charged into a flask of 10 mL, equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was stirred at a known temperature for the desired time. After the reaction, the products were analyzed by a gas chromatography (GC, Agilent 6820) and identified by GC-MS (Shimadzu QP2010).

Reusability of [(n-Bu₃Sn)₂MoO₄]

The reusability of $(n-Bu_3Sn)_2MoO_4$ was examined by the reaction of DEC and 1-hexanol at the optimized reaction conditions (130 °C, 2 h, 33 mmol DEC). The catalyst was recovered by distillation at reduced pressure, and was reused directly for the next run.

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References

- (a) A.-A. G. Shaikh and S. Sivaram, *Chem. Rev.*, 1996, 96, 951;
 (b) T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312;
 (c) J. P. Parrish, R. N. Salvatore and K. W. Jung, *Tetrahedron*, 2000, 56, 8207;
 (d) P. Tundo and M. Selva, *Acc. Chem. Res.*, 2002, 35, 706;
 (e) P. Tundo, F. Aricò, A. E. Rosamilia and S. Memoli, *Green Chem.*, 2008, 10, 1182;
 (f) C. Han and J. A. Porco, Jr., *Org. Lett.*, 2007, 9, 1517;
 (g) P. Tundo, F. Aricò, G. Gauthier, L. Rossi, A. E. Rosamimila, H. S. Bevinakatti, R. L. Sievert and C. P. Newman, *ChemSusChem*, 2010, 3, 566.
- 2 (a) Y. Ono, *Appl. Catal.*, *A*, 1997, **155**, 133; (b) J. P. Parrish, R. N. Salvatore and K. W. Jung, *Tetrahedron*, 2000, **56**, 8207.
- 3 (a) B. Schäffner, J. Holz, S. P. Verevkin and A. Börner, *Chem-SusChem*, 2008, 1, 249; (b) B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, 110, 4554.
- 4 (a) S. Gryglewicz, F. A. Oko and G. Gryglewicz, *Ind. Eng. Chem. Res.*, 2003, **42**, 5007; (b) N. Ishida, H. Hasegawa, U. Sasaki and T. Ishikawa, *U.S. Patent*, 5391311, 1995.
- 5 M. A. Pacheco and C. L. Marshall, Energy Fuels, 1997, 11, 2.
- 6 (a) M. Pianka, J. Sci. Food Agric., 1966, 17, 47; (b) M. Pianka and P. Sweet, J. Sci. Food Agric., 1968, 19, 667; (c) D. E. Hardies and J. K. Rinehart, U.S. Patent, 4022609, 1970.
- 7 (a) R. M. Burk and M. B. Roof, *Tetrahedron Lett.*, 1993, 34, 395;
 (b) G. Bertolini, G. Pavich and B. Vergani, *J. Org. Chem.*, 1998, 63, 6031;
 (c) A. R. Choppin and J. W. Rogers, *J. Am. Chem. Soc.*, 1948, 70, 2967;
 (d) K. Kondo, N. Sonoda and S. Tsutsumi, *Tetrahedron Lett.*, 1971, 12, 4885;
 (e) D. M. Fenton and P. J. Steinwand, *J. Org. Chem.*, 1974, 39, 701.
- 8 (a) Y. Kishimoto and I. Ogawa, *Ind. Eng. Chem. Res.*, 2004, **43**, 8155; (b) B. M. Bhanage, S. I. Fujita, Y. Ikushima, K. Torii and M. Arai, *Green Chem.*, 2003, **5**, 71; (c) Y. H. Chang, T. Jiang, B. X. Han, Z. M. Liu, W. Z. Wu, L. Gao, J. C. Li, H. X. Gao, G. Y. Zhao and J. Huang, *Appl. Catal.*, *A*, 2004, **263**, 179; (d) Y. Li, X. Q. Zhao and Y. J. Wang, *Appl. Catal.*, *A*, 2005, **279**, 205; (e) J.-S. Tian, C.-X. Miao, J.-Q. Wang, F. Cai, Y. Du, Y. Zhao and L.-N. He, *Green Chem.*, 2007, **9**, 566; (f) S. Fujita, B. M. Bhanage, Y. Ikushima and M. Arai, *Green Chem.*, 2001, **3**, 87.
- 9 (a) M. A. Casadei, S. Cesa and L. Rossi, *Eur. J. Org. Chem.*, 2000, 2445; (b) L. Zhang, D. Niu, K. Zhang, G. Zhang, Y. Luo and J. Lu, *Green Chem.*, 2008, **10**, 202.
- 10 (a) S.-I. Kim, F. Chu, E. E. Dueno and K. W. Jung, J. Org. Chem., 1999, 64, 4578; (b) R. N. Salvatore, V. L. Flanders, D. Ha and K. W. Jung, Org. Lett., 2000, 2, 2797.
- 11 M. O. Bratt and P. C. Taylor, J. Org. Chem., 2003, 68, 5439.
- 12 Y. R. Jorapur and D. Y. Chi, J. Org. Chem., 2005, 70, 10774.
- 13 S. Carloni, D. E. De Vos, P. A. Jacobs, R. Maggi, G. Sartori and R. Sartorio, *J. Catal.*, 2002, **205**, 199.
- 14 B. Veldurthy and F. Figueras, Chem. Commun., 2004, 734.
- 15 B. Veldurthy, J. M. Clacens and F. Figueras, *Eur. J. Org. Chem.*, 2005, 10, 1972.
- 16 M. L. Kantam, U. Pal, B. Sreedhar and B. M. Choudary, Adv. Synth. Catal., 2007, 349, 1671.
- 17 Y.-X. Zhou, S.-G. Liang, J.-L. Song, T.-B. Wu, S.-Q Hu, H.-Z. Liu and B.-X. Han, *Acta Phys. -Chim. Sin.*, 2010, 26, 1.
- 18 U. Behrens, A. K. Brimah, K. Yünlü and R. D. Fischer, Angew. Chem., Int. Ed. Engl., 1993, 32, 82.
- 19 M. Abrantes, A. Valente, M. Pillinger, I. S. Gonçalves, J. Rocha and C. C. Romão, J. Catal., 2002, 209, 237.
- 20 M. Abrantes, A. A. Valente, M. Pillinger, I. S. Gonçalves, J. Rocha and C. C. Romão, *Chem.-Eur. J.*, 2003, 9, 2685.
- 21 A. Bordoloi and S. B. Halligudi, Adv. Synth. Catal., 2007, 349, 2085.