



Short Communication

New attempt for CO₂ utilization: One-pot catalytic syntheses of methyl, ethyl and n-butyl carbamates

Jian Li, Xiujuan Qi, Liguang Wang, Yude He, Youquan Deng*

Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

ARTICLE INFO

Article history:

Received 5 February 2011

Received in revised form 24 March 2011

Accepted 11 April 2011

Available online 17 April 2011

Keywords:

Carbon dioxide

Vanadium(V)-oxide catalyst

Fixation

Alkyl carbamates

ABSTRACT

The direct production of methyl, ethyl and n-butyl carbamates (MC, EC and BC) from NH₃, CO₂ and alcohols could efficiently be catalyzed by V₂O₅, and ca. 11–25% yields with 98% selectivity for alkyl carbamates could be obtained. The catalyst could be recycled six times without obvious decrease in catalytic activity. XRD and XPS analysis showed that in-situ produced (NH₄)₂V₃O₈ was the catalytically active species.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The chemical fixation and utilization of CO₂ is of greatest interest because it is an abundant, renewable C1 feedstock [1]. Along with growing environmental concern induced by CO₂, chemical fixation of CO₂ to useful chemicals has received great attention [2]. In the past decades, many processes involving CO₂ have been explored, of which the catalytic hydrogenation of CO₂ to produce HCOOH, CH₃OH, or CH₄ has been considered the promising route of CO₂ utilization [3]. However, the limited hydrogen supply restricted their large-scale application. Up to now, the large-scale processes of CO₂ utilization are also very limited in industry [4]. Alkyl carbamates including methyl carbamate (MC), ethyl carbamate (EC) and butyl carbamate (BC) are a class of important intermediates, and are widely used as alternative carbonyl source in many carbonylation reactions [5]. They are generally produced from alcoholysis of urea or ammonolysis of dimethyl carbonate [6,7]. In view of industrial application, direct production of alkyl carbamates from CO₂ and NH₃ and alcohol is a promising process. Up to now, the studies on direct production of alkyl carbamate from NH₃, CO₂ and alcohols have been not reported yet, although syntheses of N-alkyl carbamates from amines, CO₂ and alcohols (or alkyl halides) were extensively studied [8–11].

Herein, we report for the first time the catalytic synthesis of MC, EC and BC from NH₃, CO₂ and alcohols with V₂O₅ as catalyst in the absence of dehydrant (Scheme 1). Compared to alkyl carbamate

syntheses from amines, this process is more attractive in large-scale CO₂ utilization.

2. Experimental

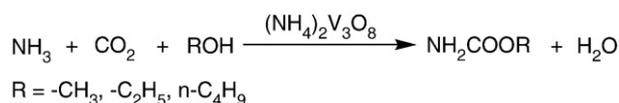
2.1. Chemicals

Alcohols were dehydrated with 4 Å molecular sieve and the commercially available metal oxides were calcined at 400 °C for 4 h before use. Other chemicals used in this work are of analytical grade and used without further purification otherwise specified. Ammonium carbamate (NH₂COONH₄) is prepared from NH₃ and CO₂ in room temperature and used as ammonia source [12]. Typically, NH₃ and CO₂ dried by 4 Å molecular sieve were pumped slowly into a three-necked flask, which filled with 500 mL anhydrous ethanol and cooled by ice-water. A white participate of NH₂COONH₄ was formed immediately. After reaction, NH₂COONH₄ was filtered and dried in a vacuum desiccator. Finally, it can be stored as a stable solid in a sealed container, and kept from heat.

2.2. Reaction procedure

All reactions were carried out in a 70 mL autoclave equipped with magnetic stirring. In a typical procedure, NH₂COONH₄ (80 mmol), alcohol (320–640 mmol) and V₂O₅ (1 mmol) were added into the autoclave and 5 MPa CO₂ was charged. The reaction was performed at 200 °C for 4 h. After cooling to room temperature, the catalyst and residual NH₂COONH₄ were separated from the mixture by filtration. The filtrate was evaporated and dried in vacuum to afford the primary product. The pure product was obtained by further re-crystallization

* Corresponding author. Tel./fax: +86 931 4968116.
E-mail address: y deng@licp.cas.cn (Y. Deng).



Scheme 1. One-pot syntheses of alkyl carbamates from CO₂, NH₂COONH₄ and alcohols catalyzed by in-situ synthesized (NH₄)₂V₃O₈ from V₂O₅.

with the alcohol. Each experiment was performed in triplicate and the standard deviations are indicated with error bars in the appropriate figures.

2.3. Identification

Qualitative analysis was conducted with a HP 6890/5973 GC–MS. Yields of alkyl carbamates were measured with an Agilent GC–6820 equipped with a FID detector and an AT.SE-54 capillary column using 1,4-dioxane as an internal standard. The ¹H NMR spectra were recorded on a Bruker AMX FT 400-MHz NMR spectrometer. X-ray diffraction (XRD) was performed on a Siemens D/max-RB powder X-ray diffractometer. Diffraction patterns were recorded with Cu K α radiation over a 2 θ range of 10° to 80° and a position-sensitive detector using a step size of 0.017°. X-ray photoelectron spectroscopy (XPS) was performed with a VG ESCALAB 210 instrument. Mg K α radiation at an energy scale calibrated versus adventitious carbon (C1s peak at 285.00 eV) was used.

2.4. Theoretical calculations

All the theoretical calculations were performed with the Gaussian 03 programs using the B3LYP functional [13]. The full electron basis set 6-31+G(d) was used for geometry optimization and frequency calculation. The optimized geometry was confirmed by the frequency calculation to be a real minimum without any imaginary vibrational frequency. And the Zero-point vibrational energy (ZPE) corrections were obtained using unscaled frequencies. The single-point electronic energies were calculated with the B3LYP/6-311++G(2df, 2p) method. With the theoretical gas-phase results in hand, we utilized the C-PCM solvation model at the B3LYP/6-31+G(d) level to estimate the solvation effect.

3. Results and discussion

The main purpose of this work is to develop a new process of CO₂ and NH₃ for syntheses of valuable chemicals. However, it is difficult to control the amount of the charged gases for each time if CO₂ and NH₃ are introduced into the autoclave together. Fortunately, it has been reported that a white solid NH₂COONH₄ can easily form when NH₃ and CO₂ are fixed. Therefore, in this paper NH₂COONH₄ was used as the feed for the purpose of ensuring the NH₃ amount consistent for each time. Firstly, MC production was used as a model reaction to evaluate the activity of different metal oxides, and the results were shown in Table 1. The blank experiment showed that only 2% of MC yield could be obtained (entry 1). Then a series of metal oxides were screened as the catalysts for the MC synthesis (entries 2–13). 4–25% MC yields could be obtained while the MC selectivity is up to 98%. Only trace of methyl N-methyl carbamate as byproduct, which may be derived from the side reaction between MC and methanol, was detected by GC–MS. Among the metal oxides tested, V₂O₅ showed the highest catalytic activity. XRD and XPS analysis showed that (NH₄)₂V₃O₈ was in-situ produced from V₂O₅ during the reaction. The reaction conditions including the reaction time, temperature, and CO₂ pressure were optimized after the catalysts screening. The most optimized conditions is as follows: NH₂COONH₄ 80 mmol, V₂O₅ 1 mmol, methanol 640 mmol, initial CO₂ pressure 5 MPa, 220 °C, 4 h

Table 1
Catalyst screening for synthesis of methyl carbamate.

Entry	Catalyst	Time/h	Tem./°C	Yield/% ^a	Sel./%	TON ^b
1	–	12	200	<2	–	–
2	MgO	12	200	4	99	6
3	CaO	12	200	6	99	10
4	Bi ₂ O ₃	12	200	9	99	14
5	CeO ₂	12	200	11	98	18
6	TiO ₂	12	200	8	99	13
7	ZrO ₂	12	200	8	99	13
8	Cr ₂ O ₃	12	200	6	99	10
9	Fe ₂ O ₃	12	200	10	99	16
10	ZnO	12	200	19	98	30
11	Co ₂ O ₃	12	200	17	98	27
12	NiO	12	200	21	98	34
13	V ₂ O ₅	12	200	25	98	40
14	V ₂ O ₅	2	200	21	98	34
15	V ₂ O ₅	4	200	24	98	38
16	V ₂ O ₅	24	200	24	96	38
17	V ₂ O ₅	4	170	13	99	21
18	V ₂ O ₅	4	180	22	98	35
19	V ₂ O ₅	4	220	21	76	33
20 ^c	V ₂ O ₅	4	200	11	99	18
21 ^d	V ₂ O ₅	4	200	18	98	29
22 ^e	V ₂ O ₅	6	180	63	96	101
23 ^f	V ₂ O ₅	4	200	18	98	29

NH₂COONH₄ 80 mmol (6.24 g, 160 mmol ammonia), V₂O₅ 1 mmol, methanol 640 mmol, initial CO₂ pressure 5 MPa.

^a GC yield based on ammonia.

^b Mol of MC produced per mol of catalyst.

^c Initial CO₂ pressure 1 MPa.

^d Initial CO₂ pressure 3 MPa.

^e Trimethoxymethane (160 mmol) as dehydrant, tetrabutylammonium bromide as cocatalyst.

^f Catalyst was recovered and used for the sixth time.

(entries 14–21). Under above conditions, 25% of MC yield with a selectivity of 98% can be achieved. Moreover, in order to obtain higher MC yield, an attempt of using several dehydrants was also made. If 4 Å molecular sieves, anhydrous sodium sulfate, and anhydrous magnesium sulfate were used, however, no any improvement in MC yield could be observed. When trimethoxymethane as dehydrant and tetrabutylammonium bromide as cocatalyst were used, ca. 63% of MC yield with 96% selectivity could be obtained (entry 22). The reusability of the catalyst showed that V₂O₅ could be recycled six times without obvious activity loss (entry 23).

In order to find out true catalytically active species, the catalytic activity of V₂O₅ and (NH₄)₂V₃O₈ was comparatively investigated. When the reaction proceeded for 0.5 h, only <1% MC yield was obtained, while ca. 4% MC was produced over the (NH₄)₂V₃O₈ under the same conditions (Fig. 1). After 1 h, the MC yield increased to 7% for the V₂O₅ and a small amount of (NH₄)₂V₃O₈ formed. After 4 h, a similar MC yield of about 24–25% could be obtained over both catalysts, indicating that in-situ produced (NH₄)₂V₃O₈ was the true catalytically active species for this reaction. Moreover, the catalytic syntheses of EC and BC over V₂O₅ were also studied. Under optimized conditions, 7% of yields for both EC and BC could be obtained after 4 h (Table 2, entries 1 and 2). After 12 h, 11% of EC yield and 14% of BC yield could be obtained.

Fig. 2. gave the XRD patterns of three materials. From Fig. 2a, seven distinct reflection peaks in the range of 15° to 35° can be attributed to the characteristic orthorhombic phase of V₂O₅, i.e. *d*₂₀₀, *d*₀₀₁, *d*₁₀₁, *d*₁₁₀, *d*₃₀₁, *d*₀₁₁ and *d*₃₁₀ spacing (ICSD Powder Diffraction File, card No. 77-2418, cell parameters *a* = 11.51, *b* = 3.564, *c* = 4.368 Å) [14]. Fig. 2b gives the *d*₀₀₁, *d*₂₁₀, *d*₂₀₁, *d*₂₁₁, *d*₃₁₀, *d*₃₁₁ and *d*₃₁₂ spacing of the typical tetragonal phase of (NH₄)₂V₃O₈ at 15° < 2 θ < 46° (ICSD Powder Diffraction File, card No. 78-1229, cell parameters *a* = 8.885, *c* = 5.564 Å) [15]. Fig. 3. gave the XP spectra of the fresh V₂O₅ and in-situ formed (NH₄)₂V₃O₈. The C, O, V elements for V₂O₅ and C, N, O, V elements for (NH₄)₂V₃O₈ can be observed. In Fig. 3A, the binding

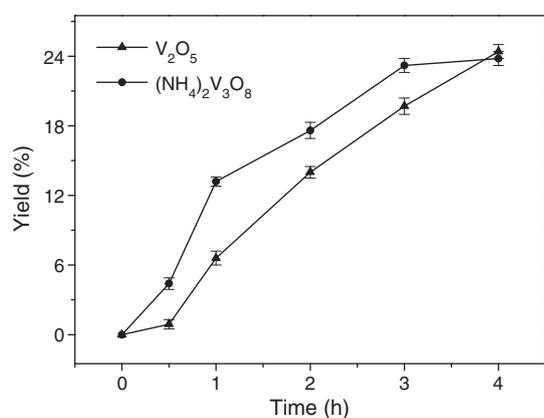


Fig. 1. Dependence of MC yields on different catalysts. Reaction condition: $\text{NH}_2\text{COONH}_4$, 80 mmol; methanol, 640 mmol; V_2O_5 , 1 mmol; $(\text{NH}_4)_2\text{V}_3\text{O}_8$, 0.67 mmol; initial CO_2 pressure, 5 MPa; 200 °C.

energy of V 2p of $(\text{NH}_4)_2\text{V}_3\text{O}_8$ is lower than that in fresh V_2O_5 . The binding energy of V 2p_{3/2} of fresh V_2O_5 is 517.7 eV, which is consistent with the literature and shows the +5 oxidation state of vanadium species [16]. The binding energy of V 2p_{3/2} for $(\text{NH}_4)_2\text{V}_3\text{O}_8$ is 517.2 eV, which is between those of V 2p_{3/2} for V_2O_5 and VO_2 . As shown in Fig. 3B, the peak of V 2p_{3/2} can be deconvoluted by two pronounced lines at 517.5 and 516.3 eV, which agrees with the +5 and +4 vanadium species in V_2O_5 and VO_2 , respectively. The peak area ratio of +5 to +4 vanadium species is 1.91, which is consistent with the $\text{V}^{5+}/\text{V}^{4+}$ ratio in $(\text{NH}_4)_2\text{V}_3\text{O}_8$. Judging from the above analysis, we can conclude that $(\text{NH}_4)_2\text{V}_3\text{O}_8$ formed from V_2O_5 and NH_3 during the reaction and V_2O_5 can be regenerated and reused from the $(\text{NH}_4)_2\text{V}_3\text{O}_8$ after calcination.

Thermodynamics calculations were also conducted to study the theoretical yields. After obtaining the $\Delta_r G$ at 200 °C and 25 MPa, the corresponding equilibrium constant K could be calculated by the Van't Hoff equation, employing a linear least-squares treatment of $\ln K$ vs $T - 1$ in Eq. (1)

$$\Delta_r G = -RT \ln K. \quad (1)$$

Then the equilibrium conversion a_{NH_3} for the syntheses of alkyl carbamates can be determined by Eq. (2)

$$K = \frac{a_{\text{NH}_2\text{COOR}} a_{\text{H}_2\text{O}}}{a_{\text{CO}_2} a_{\text{NH}_3} a_{\text{ROH}}}. \quad (2)$$

Considering the complexity of the reaction conditions (200 °C, 25 MPa), an approximation was adopted in the above equation, in which the molar ratio was used as a substitution of the ratio of activities.

Effect of reaction temperature and pressure on $\Delta_r G$ for the synthesis of alkyl carbamates was investigated by theoretical calculations and the

Table 2
Screening alcohols for synthesis of alkyl carbamates.

Entry	Alcohols	Time/h	Sel./%	Yield/% ^a
1	EtOH	4	99	7
2	n-BuOH	4	99	7
3	EtOH	12	99	11
4	n-BuOH	12	99	14
5	EtOH	20	98	12
6	n-BuOH	20	97	14

$\text{NH}_2\text{COONH}_4$ (80 mmol), V_2O_5 (1 mmol), ethanol (480 mmol), n-butanol (320 mmol), initial CO_2 pressure 5 MPa, 200 °C.

^a GC yield based on the ammonia added with an internal standard.

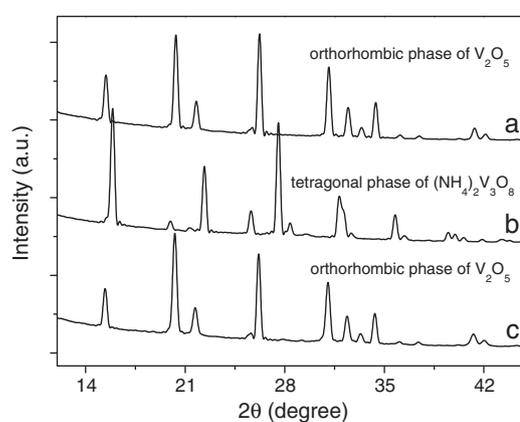


Fig. 2. XRD spectra of catalysts: (a) fresh V_2O_5 , (b) $(\text{NH}_4)_2\text{V}_3\text{O}_8$ after reaction, and (c) V_2O_5 prepared from $(\text{NH}_4)_2\text{V}_3\text{O}_8$ by calcined at 500 °C.

results are illustrated in Fig. 4. At 25 °C and 1 atm, the reaction for the synthesis of alkyl carbamates was an exothermic process and did not occur spontaneously ($\Delta_r H_{\text{mc}} = 1.45$ kJ/mol, $\Delta_r G_{\text{mc}} = 28.4$ kJ/mol). The $\Delta_r G$ increased with the elevation of the temperature (Fig. 4a) and decreased with the increase of the reaction pressure (Fig. 4b), which indicated that decreasing the temperature and increasing the pressure should be beneficial to this reaction. However, the $\Delta_r G$ for the synthesis of MC, EC and BC were still 11.66–16.09 kJ/mol at 200 °C and 25 MPa, which illuminated that this reaction was difficult to occur even under rigorous conditions. After that the equilibrium constant K was calculated by Eq. (1) under these reaction conditions.

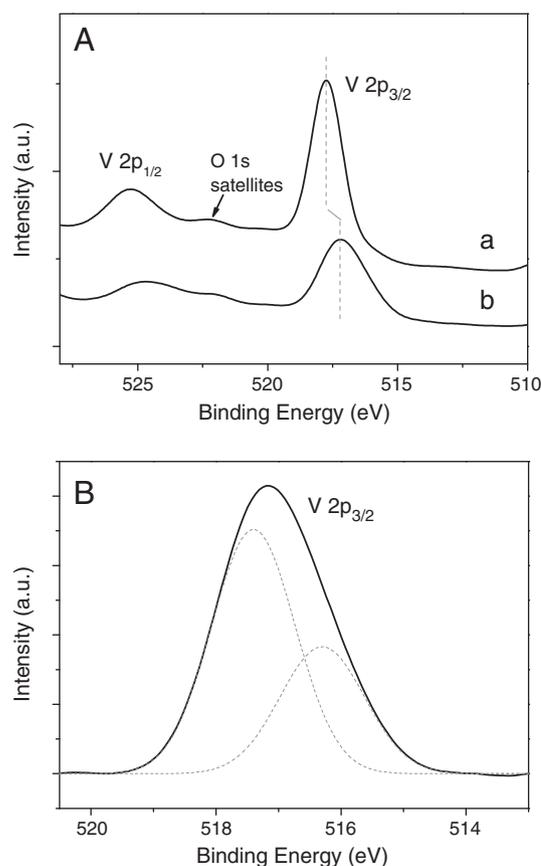


Fig. 3. XP spectra of (A) V 2p for (a) V_2O_5 and (b) $(\text{NH}_4)_2\text{V}_3\text{O}_8$, and fitting curve of (B) V 2p_{3/2} for $(\text{NH}_4)_2\text{V}_3\text{O}_8$.

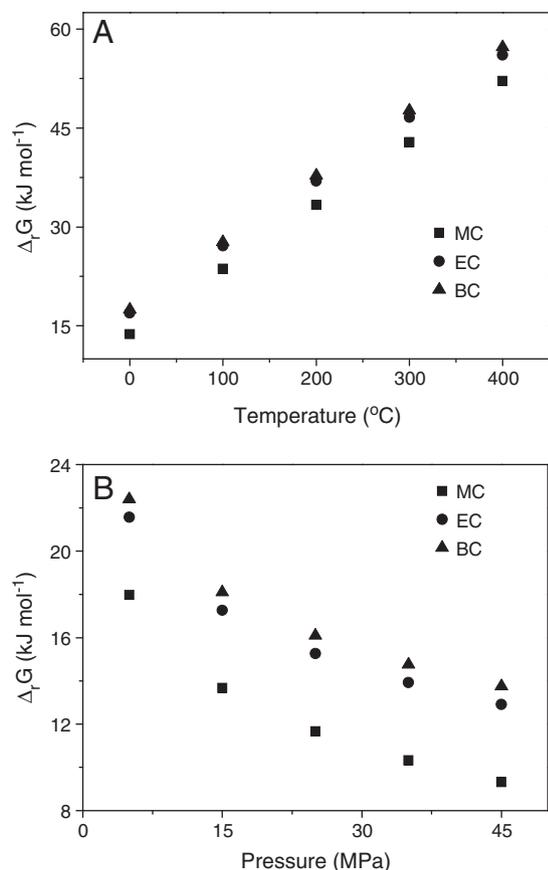


Fig. 4. Effect of reaction temperature (A) and pressure (B, 200 °C) on $\Delta_r G$ for synthesis of alkyl carbamates.

Under the experimental molar ratio of substrates, the equilibrium conversion of NH_3 under different reaction pressure at 200 °C was calculated based on Eq. (2) and the result is shown in Fig. 5. The equilibrium conversion of NH_3 increased with the raise of the reaction pressure. Theoretical equilibrium conversions of 29%, 19% and 16% of NH_3 can be obtained for syntheses of MC, EC and BC at 200 °C and 25 MPa. For the experiment results, 25% yield for MC was obtained, which is close to the theoretical value, i.e. 29%. This also showed that $(\text{NH}_4)_2\text{V}_3\text{O}_8$ was an efficient catalyst for this reaction.

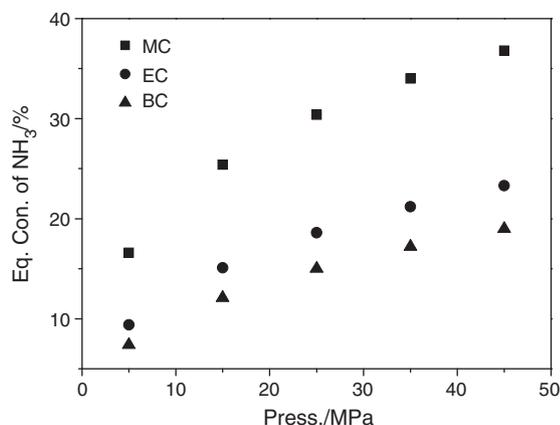


Fig. 5. Dependence of the equilibrium conversion of NH_3 on reaction pressures at 200 °C.

4. Conclusion

One-pot production of alkyl carbamates from $\text{NH}_2\text{COONH}_4$, CO_2 and alcohols could be catalyzed over V_2O_5 catalyst, and ca. 25% MC yield with 98% selectivity could be obtained. This catalyst also exhibited good catalytic activity for the production of EC and BC. XRD and XPS analysis as well as the contrast experiments showed that in-situ produced $(\text{NH}_4)_2\text{V}_3\text{O}_8$ was the true catalytically active species for this reaction. Thermodynamics calculations showed that this reaction was difficult to occur even in rigorous conditions, and theoretical equilibrium conversion for the synthesis of MC is only 29% at 200 °C and 25 MPa. As a result, 25% MC yield obtained from the experiment showed V_2O_5 was an efficient catalyst for this reaction. This also provides a new concept of CO_2 utilization in industry.

Acknowledgment

The computing part of this work was supported by supercomputing center, Computer Network Information Center (CNIC), Chinese Academy of Sciences (CAS).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.04.008.

References

- [1] M. Mikkelsen, M. Jorgensen, F.C. Krebs, *Energy Environ. Sci.* 3 (2010) 43.
- [2] T. Sakakura, J.C. Choi, H. Yasuka, *Chem. Rev.* 107 (2007) 2365.
- [3] F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro, F. Frusteri, *J. Catal.* 249 (2007) 185.
- [4] C.A. Tsipis, P.A. Karipidis, *J. Phys. Chem. A* 109 (2005) 8560.
- [5] H.Z. Zhang, X.G. Guo, Q.H. Zhang, Y.B. Ma, H.C. Zhou, J. Li, L.G. Wang, Y.Q. Deng, *J. Mol. Catal. A: Chem.* 296 (2008) 36.
- [6] Y. Ono, *Appl. Catal. A: Gen.* 155 (1997) 133.
- [7] Y.Q. Deng, Y.B. Ma, L.G. Wang, X.G. Guo, S.G. Zhang, Y.D. He, W. Stefan, K. Stephan, Z.P. Zhou, WO Patent 2009106237(A2) (2009).
- [8] M. Abla, J.C. Choi, T. Sakakura, *Chem. Commun.* (2001) 2238.
- [9] M. Abla, J.C. Choi, T. Sakakura, *Green Chem.* 6 (2004) 524.
- [10] A. Ion, C.V. Doorslaer, V. Parvulescu, P. Jacobs, D.D. Vos, *Green Chem.* 10 (2008) 111.
- [11] M.A. Casadei, A. Inesi, F.M. Moracci, L. Rossi, *Chem. Commun.* (1996) 2575.
- [12] R.N. Bennett, P.D. Ritchie, D. Roxburgh, J. Thomson, *Trans. Faraday Soc.* 49 (1953) 925.
- [13] M.J. Frisch, G.W. Trucks, C. Gonzalez, J.A. Pople, et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- [14] T. Ono, Y. Tanaka, T. Takeuchi, K. Yamamoto, *J. Mol. Catal. A: Chem.* 159 (2000) 293.
- [15] T.Z. Ren, Z.Y. Yuan, X.D. Zou, *Cryst. Res. Technol.* 42 (2007) 317.
- [16] C.D. Wagner, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Minnesota, 1979 p. 74.