Res Chem Intermed
DOI 10.1007/s11164-013-1030-6

Synthesis and characterization of bis[2-(1*H*-benzimidazol-2-yl)benzoato]nickel(II), and its use for preparation of dimethyl carbonate from methanol and CO_2

Yanning Shi · Xilang Jin · Yechen Hu · Shuli Wang · Jianli Li · Zhen Shi

Received: 12 November 2012 / Accepted: 7 January 2013

Abstract A new complex, bis[2-(1*H*-benzimidazol-2-yl)benzoato]nickel(II) (NiL_2), has been synthesized and characterized. It was used as catalyst for synthesis of dimethyl carbonate (DMC) from methanol and CO_2 in the presence of dicyclohexyl carbodiimide (DCC) as promoter. The effects of temperature, reaction time, and amount of catalyst on the reaction, and the reusability of the catalyst, were investigated. A catalytic mechanism is proposed. The results revealed that NiL_2 + DCC had excellent catalytic activity, because this catalytic system promoted facile formation of DMC, with acceptable yield, in the presence of a small amount of NiL_2 and under moderate conditions (80 °C, 1.0 MPa). Moreover, the catalyst has been consecutively used five times without significant loss of activity.

Keywords Dimethyl carbonate · Methanol · NiL_2 · DCC

Introduction

Dimethyl carbonate (DMC) is an important compound in so-called green chemistry. DMC is very important as an environmentally benign synthetic reagent because it works as a nontoxic substitute for phosgene, dimethyl sulfate, and methyl halides in methylation and carbonylation processes [1]. DMC can also be used as an environmentally friendly fuel additive and as a polar solvent [2, 3]. Currently, several processes have been proposed for industrial synthesis of DMC, including the methanolysis of phosgene [4], oxidative carbonylation of methanol [5], and

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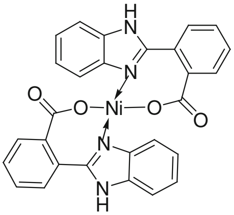
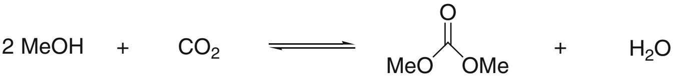
Electronic supplementary material The online version of this article (doi:10.1007/s11164-013-1030-6) contains supplementary material, which is available to authorized users.

Y. Shi · X. Jin · Y. Hu · S. Wang · J. Li (✉) · Z. Shi
Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education,
College of Chemistry and Materials Science, Northwest University, Xi'an 710069, Shaanxi, China
e-mail: lijianli@nwu.edu.cn

Fig. 1 The proposed structure of NiL_2

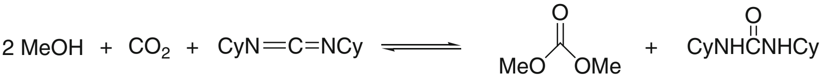


transesterification [6]. However, these processes have disadvantages. In contrast, synthesis of DMC from methanol and CO_2 (Eq. 1) is an interesting alternative synthetic method from the perspectives of both atom economy and risk reduction [7].



$$2\,\mathrm{MeOH} + \mathrm{CO_2} \rightleftharpoons \mathrm{MeO{-}C({=}O){-}OMe} + \mathrm{H_2O} \qquad (1)$$

This method of synthesis of DMC is appealing environmentally but poses significant challenges, because the reaction is thermodynamically quite unfavorable. To circumvent this problem, several promoters, for example dimethoxypropane (DMP) [8], acetals [9], and molecular sieves [10], have been used as dehydrating reagents for this process to remove water and thus facilitate formation of DMC. Recently dicyclohexyl carbodiimide (DCC) has been found to be a very active promoter under milder conditions [11]. The effectiveness of this promoter is attributed to conversion of carbodiimide into the relevant urea (Eq. 2). This also makes the overall reaction thermodynamically more favorable. A variety of catalysts have been used for direct synthesis of DMC, including organometallic compounds [12], ZrO_2 [13], heteropolyacid [14], and supported Cu–Ni bimetal catalysts [15].



$$2\,\mathrm{MeOH} + \mathrm{CO_2} + \mathrm{CyN{=}C{=}NCy} \rightleftharpoons \mathrm{MeO{-}C({=}O){-}OMe} + \mathrm{CyNH\overset{O}{\overset{\|}{C}}NHCy} \qquad (2)$$

It has been reported that $Ni(OAc)_2$ has good catalytic activity in CO_2-based carboxylation of methanol [16]. DMC can be produced with high yield and selectivity when the synthesis is conducted under near supercritical conditions. This rigorous method is difficult to control, however. In the course of studying the synthesis of DMC from CH_3OH and CO_2, we found that NiL_2 (Fig. 1) was an effective catalyst for formation of DMC in the presence of DCC (as promoter). The catalyst promoted facile formation of DMC at 80 °C and moderate pressure of CO_2 (1.0 MPa) with high yield.

In this paper, we describe the synthesis and characterization of NiL_2, which has proved to be an excellent catalyst in the one-step synthesis of DMC. The effect on the process of temperature, reaction time, and amount of catalyst, and the reusability of the catalyst, have been investigated. A catalytic mechanism has been proposed.

Experimental

Reagents and characterization techniques

o-Phthalic acid, *o*-phenylenediamine, PPA, DCC, NaOH, $Ni(OAc)_2{\cdot}4H_2O$, $NiCl_2{\cdot}6H_2O$, $NiSO_4{\cdot}7H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and methanol were all analytical-reagent or guaranteed-reagent-grade. CO_2 was 99.999 % pure.

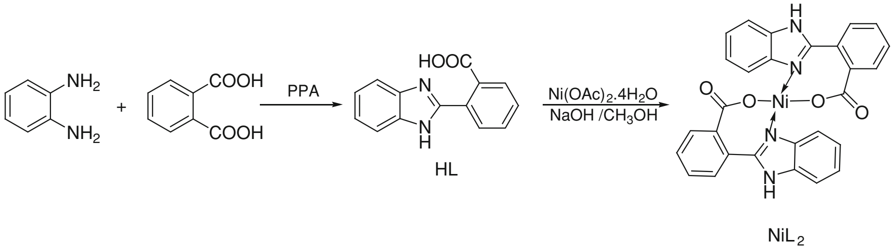
Elemental analysis (C, H, and N) was performed with a Vario EL-III CHNOS instrument. FT-IR spectra in the range 4,000–400 cm^{-1} were recorded on a Bruker Equinox-550 spectrophotometer, using the KBr pellet technique. ^1H and ^{13}C NMR spectra were obtained at room temperature by use of a Varian Inova 400 MHz apparatus and tetramethylsilane (TMS) for reference. Molecular weights were measured by electrospray ionization mass spectrometry (ESI-MS).

Catalyst preparation

The catalyst was prepared by reaction of $Ni(OAc)_2{\cdot}4H_2O$ with 2-(1*H*-Benzimidazol-2-yl)benzoic acid. The ligand was synthesized by polyphosphoric acid (PPA)-catalyzed condensation of *o*-phthalic acid with *o*-phenylenediamine [17] (Scheme 1).

Synthesis of 2-(1*H*-benzimidazol-2-yl)benzoic acid (HL)

o-Phenylenediamine (10.8 g, 0.1 mol) and *o*-phthalic acid (16.6 g, 0.1 mol) were mixed with a sufficient quantity of PPA to give a stirrable paste. The mixture was heated slowly to 250 °C, and the resulting solution was stirred at 250 °C for 4 h, left to cool to approximately 100 °C, and poured into a large volume of rapidly stirred water. The mixture was then cooled on ice and made alkaline by the addition of 50 % sodium hydroxide solution. The alkaline slurry was isolated by filtration, dried, and recrystallized from suitable solvents. Yield: 71 %. MP: 278 °C. FT-IR: ν, cm^{-1}, 3355, 2739, 1625, 1538, 1490, 1448, 1319, 1283, 1152, 1117, 1001, 920, 860, 829, 786, 749, 707, 648, 523, 479. ^1H NMR (400 MHz, DMSO-d_6) δ 8.22 (s, 1H), 7.89 (s, 1H), 7.65 (m, 3H), 7.50–7.25 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.77, 144.53,.144.37, 140.87, 140.70, 135.83, 133.70, 124.19.



Scheme 1 Preparation of the catalyst NiL_2

Synthesis of Ni complex (NiL_2)

HL (0.476 g, 2.0 mmol) and NaOH (0.080 g, 2.0 mmol) were dissolved in a sufficient amount of methanol, then $Ni(OAc)_2 \cdot 4H_2O$ (0.249 g, 1.0 mmol) in 20 ml methanol was added to this solution with stirring. The product began to precipitate from the solution. After 1 h at room temperature, the solid was isolated by filtration, washed with methanol, and air-dried. The yield was 82 %. Anal calcd. for $C_{28}H_{18}N_4NiO_4$ %: C 63.08, H 3.40, N 10.51; found C 62.95, H 3.32, N 10.63. HRMS (ESI): calcd. for $C_{28}H_{18}N_4NiO_4$: 533.0754 (M + H); found: 533.0748. FT-IR: ν, cm^{-1}, 3423, 1619, 1561, 1493, 1435, 1380, 1324, 1285, 1229, 1140, 1092, 1004, 880, 810, 746, 650, 588, 481, 435, 417.

DMC synthesis

High-pressure reactions were conducted in a 250-ml stainless steel autoclave equipped with a mechanical stirrer. The reaction temperature was monitored by means of an internal thermocouple. General procedure for synthesis of DMC from methanol and CO_2 [18]: methanol (32.00 g, 1 mol), NiL_2 (0.53 g, 1.0 mmol), and DCC (2.06 g, 10 mmol) were placed in the autoclave, which was sealed and flushed with CO_2 three times, then pressurized to 1.0 MPa. The mixture was stirred at the desired temperature. After a reaction time of 6 h, the reactor was cooled to room temperature, and pressure was gently released. Reaction products were separated and quantitatively analyzed by GC (capillary column) with flame ionization detection (FID), with *n*-butyl alcohol as internal standard. All the volatile products were also characterized with GC–MS using a Shimadzu GC-2010 gas chromatograph connected to a GCMS-QP 2010 Plus mass spectrometer.

Results and discussion

Structural characterization of the catalyst

The IR spectrum of HL contains a strong ν_{N-H} stretching band at 3,355 cm^{-1}. A broad absorption band at 3,200–2,500 cm^{-1} is attributed to intramolecular hydrogen bonding. Bands at 1625, 920, and 749 cm^{-1} were attributed to $\nu_{C=O}$, δ_{OH}, and the four adjacent H atoms in the phenyl ring, respectively. ^1H NMR and ^{13}C NMR spectra of HL were also consistent with the structure.

The ν_{OH}, $\nu_{C=O}$, and δ_{OH} absorption bands are not observed in the IR spectrum of NiL_2, indicating Ni–O bond formation. There is a shift of the C=N vibration to lower frequencies (1,619 cm^{-1}), which is ascribed to *N*–metal coordination. The presence of bands at 435 and 481 cm^{-1} for NiL_2, ascribed to ν_{Ni-O} and ν_{Ni-N} vibrations, respectively, are conclusive evidence of bonding of the oxygen and nitrogen atoms to the nickel ion. HRMS data of for NiL_2 correspond perfectly to the expected $[M + H]^+$ *m*/*z* value. From these results and similar complexes reported in literature [19], it can be concluded that the HL is coordinated to the metal ion via the

Table 1 Catalytic activity of NiL_2

Entry	Catalyst[a]	Promoter	DMC yield[b] (%)
1	$Ni(OAc)_2$	None	0
2	NiL_2	None	0
3	$Ni(OAc)_2$	DCC	11
4	$NiCl_2$	DCC	10
5	$NiSO_4$	DCC	9
6	$Ni(NO_3)_2$	DCC	10
7	NiL_2	DCC	34

Reaction conditions: CH_3OH (1.0 mol), CO_2 (1.0 MPa), catalyst (1 mmol), DCC (10 mmol), 70 °C, 6 h

[a] $Ni(OAc)_2$, $NiCl_2$, $NiSO_4$, and $Ni(NO_3)_2$ were obtained from $Ni(OAc)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, respectively

[b] Based on DCC

phenolate oxygen and the imidazole nitrogen atoms; the proposed structure of the complex is depicted in Fig. 1.

Catalytic activity of NiL_2

The catalytic activity of NiL_2 was tested in the synthesis of DMC from methanol and CO_2. Obviously, as shown in Table 1, NiL_2 alone cannot drive the reaction under these conditions. The same was observed for $Ni(OAc)_2$. This is because the reaction is thermodynamically quite unfavorable. To identify the optimum catalyst for the reaction promoted by DCC, several nickel salts were examined, including $Ni(OAc)_2$, $NiCl_2$, $NiSO_4$, and $Ni(NO_3)_2$. However, they had much lower activity (entries 3–6). In contrast, remarkable enhancement of catalytic activity was observed for NiL_2 (entry 7).

Effect of reaction temperature on formation of DMC

The effect of reaction temperature on the formation of DMC was investigated in the range 50 to 100 °C. The results, presented in Table 2, show that a lower reaction temperature is more favorable for DMC formation, and maximum yield of DMC was observed at 80 °C. This result is in agreement with thermodynamic calculation and with those reported in literature [16, 20].

Effect of reaction time on the formation of DMC

Results from study of the effect of reaction time on the yield of DMC are listed in Table 3. Experiments showed that the yield of DMC rapidly increased up to 3 h. This result indicates that NiL_2–DCC enables very effective formation of DMC. When the reaction time was longer than 3 h, the yield of DMC decreased. This is because of decomposition of DCC and reversal of the equilibrium.

Table 2 Effect of temperature on the formation of DMC

Entry	Temp. (°C)	DMC yield[a] (%)
1	50	18
2	60	26
3	70	34
4	80	47
5	90	40
6	100	33

Reaction conditions: CH_3OH (1.0 mol), CO_2 (1.0 MPa), NiL_2 (1 mmol), DCC (10 mmol), 6 h

[a] Based on DCC

Table 3 Effect of reaction time on the formation of DMC

Entry	Reaction time (h)	DMC yield[a] (%)
1	2	42
2	3	58
3	6	47
4	9	32
5	12	31
6	24	21

Reaction conditions: CH_3OH (1.0 mol), CO_2 (1.0 MPa), NiL_2 (1 mmol), DCC (10 mmol), 80 °C

[a] Based on DCC

Effect of amount of catalyst on the formation of DMC

Table 4 summarizes the effect of the amount of catalyst on the synthesis of DMC. It was found that use of 0.5 mmol NiL_2 resulted in maximum yield of DMC. When the amount of catalyst was increased beyond 0.5 mmol, the yield of DMC remained stable. This indicates that 0.5 mmol catalyst was sufficient to obtain DMC in good yield under the conditions specified.

Reusability of the catalyst in the formation of DMC

The reusability of catalysts is one of the important benefits of large-scale operations and commercial applications. Therefore, we investigated the reusability of NL_2 in the synthesis of DMC from methanol and CO_2. Significant loss of the catalytic activity was not observed even after five runs (Table 5). The catalyst can be recovered by simple filtration, washing, and drying at 60 °C.

Table 4 Effect of amount of catalyst on the formation of DMC

Entry	Amount of catalyst (mmol)	DMC yield[a] (%)
1	0.25	27
2	0.5	61
3	1	58
4	2	60
5	4	59

Reaction conditions: CH_3OH (1.0 mol), CO_2 (1.0 MPa), DCC (10 mmol), 80 °C, 3 h

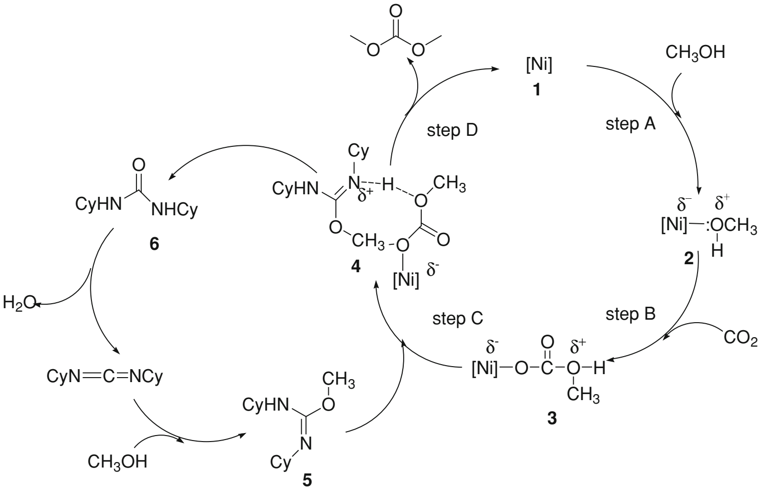
[a] Based on DCC

Table 5 Reusability of the catalyst in the formation of DMC

Entry	Run no.	DMC yield[a] (%)
1	1	61
2	2	60
3	3	59
4	4	58
5	5	58

Reaction conditions: CH_3OH (1.0 mol), CO_2 (1.0 MPa), NiL_2 (0.5 mmol), DCC (10 mmol), 80 °C, 3 h

[a] Based on DCC



Scheme 2 The proposed catalytic reaction mechanism

Proposed reaction mechanism

On the basis of the experimental results and the literature [11, 16], we proposed a plausible catalytic cycle (Scheme 2). In step A, [Ni] **1** is regarded as the catalytic species for activation of methanol. Step B is insertion of CO_2 into an Ni–O bond with formation of **3**. At the same time, addition of methanol to the cumulene forms *o*-methylisourea **5** that may further interact with **3** to form **4**. The last step is conversion of **4** into DMC and urea **6** with regeneration of the catalyst. The urea **6** can also be reconverted into DCC [21].

Conclusions

In summary, we have developed a new catalytic system for formation of DMC from methanol and CO_2. The experimental results show that NiL_2–DCC had excellent catalytic activity, because the catalytic system, containing a small amount of NiL_2, promoted facile formation of DMC under moderate conditions (80 °C, 1.0 MPa) with an acceptable yield. The NiL_2 could be easily synthesized, recovered simply, and consecutively reused. The reaction described in this article may further be developed for application to the synthesis of DMC.

Acknowledgments This work was supported by the National Natural Science Foundation of China (nos 20972124, 21272184), the Shaanxi Science and Technology Co-ordination Innovation Engineering Project (No. 2011K12-77), the Special Science Research Foundation of Education Committee in Shaanxi Province (No. 12JK0584), and the Xi'an City Science and Technology Project (No. CXY1123-1).

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