



Synthesis of dialkyl hexamethylenedicarbamate from 1,6-hexamethylenediamine and alkyl carbamate over $Y(NO_3)_3 \cdot 6H_2O$ catalyst

Hongzhe Zhang^{a,b}, Xiaoguang Guo^{a,b}, Qinghua Zhang^{a,b}, Yubo Ma^{a,b},
Hancheng Zhou^a, Jian Li^{a,b}, Ligu Wang^{a,b}, Youquan Deng^{a,*}

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

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:

Received 26 May 2008

Accepted 15 August 2008

Available online 11 September 2008

Keywords:

Green chemistry

Alkyl carbamate

Dialkyl hexamethylenedicarbamate

1,6-Hexamethylenediamine

Non-phosgene

ABSTRACT

The non-phosgene carbonylation of 1,6-hexamethylenediamine (HDA) with alkyl carbamates using $Y(NO_3)_3 \cdot 6H_2O$ as a catalyst and the influence of reaction variables on the yields of dialkyl hexamethylenedicarbamate (HDC) were studied. At 453 K and in the presence of 5 wt.% $Y(NO_3)_3 \cdot 6H_2O$, nearly 100% HDA conversion and 85% dibutyl hexamethylenedicarbamate (BHDC) isolated yield could be achieved when butyl carbamate (BC) was employed as a carbonyl source. During reaction, an induction period was observed, but it almost disappeared by pretreating the catalyst with *n*-butanol. The FT-IR, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) characterizations of the catalyst showed that some transformation occurred when the catalyst was pretreated with *n*-butanol or employed during reaction, i.e., part decomposition of $Y(NO_3)_3$ to Y_2O_3 , conversion from crystal to amorphous state, changes occurring in chemical state of the active species, as well as some subtle interactions between the catalyst and *n*-butanol. All these observed changes might be the reason resulting in activation of the catalyst.

© 2008 Published by Elsevier B.V.

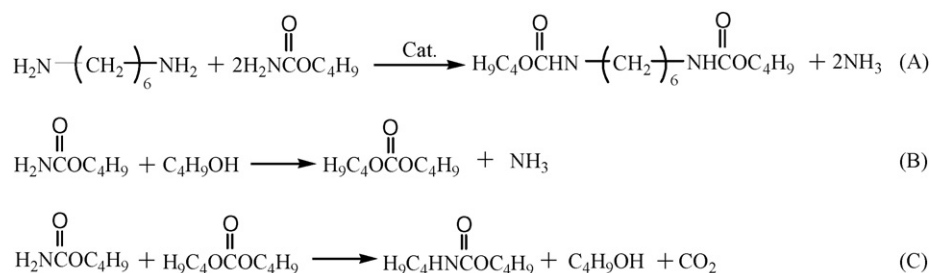
1. Introduction

Isocyanates have great commercial importance in the manufacture of polyurethanes [1–4]. They are commercially synthesized by direct reaction of phosgene with amines. This method poses great concerns for both environmental and safety problems. Not only is phosgene itself an extremely toxic reagent, but also HCl released as a byproduct causes serious corrosion. Along with the increasing attention of environment problems, to develop environmentally friendly processes for synthesis of isocyanates is highly desirable. Among several developed non-phosgene routes [5–9], the most promising one includes two steps: (1) to synthesize carbamates by non-phosgene carbonylation of *N*-containing compounds, and (2) to achieve the desired isocyanates by thermal decomposition of the corresponding carbamates [10–14]. Since the thermal decomposition technique has been well developed in industry, to develop efficient non-phosgene carbonylation processes of acquiring carbamates has become the key step for the above non-phosgene route. To achieve this target, great endeavors have been made and several alternative non-phosgene carbonyl sources for producing carbamates have been developed, i.e., CO [15], CO₂ [16], organic

carbonates (especially DMC) [17], etc. For these phosgene alternatives, many new problems also exist. For example, the use of CO not only can not achieve the industrially practicable results but also is poisonous and easily explosive when mixing with O₂ in oxidative carbonylation to carbamates; Using CO₂ directly to synthesize carbamates is very difficult due to the chemical inertness of CO₂; From the view of environment, DMC is a green replacer of phosgene and can also be used in non-phosgene synthesis of carbamates, however, in addition of the separation problem of methanol–DMC azeotrope, it is also not feasible industrially considering its expensive cost.

Moreover, the utilization of alkyl carbamates (e.g., methyl carbamate (MC), ethyl carbamate (EC) and BC) as environmentally friendly carbonyl source for non-phosgene carbonylation also attracted chemists' attention [18,19]. Compared with DMC, CO₂, and CO, it possesses several advantages: (1) more easily available in large amounts from industry than DMC, (2) relatively higher activity than CO₂, (3) more safer than CO, and (4) easier to be stored as solid than the gas. However, the reports for producing carbamates, in particular yielding dialkyl hexamethylenedicarbamate (HDC, an important precursor of 1,6-diisocyanatohexane), are still very limited, and meanwhile, rigorous reaction conditions such as high temperature (>473 K) or long reaction time (>10 h) are always needed in these reports [20,21]. Based on our continuous efforts to develop non-phosgene processes

* Corresponding author. Tel.: +86 931 4968116; fax: +86 931 4968116.
E-mail address: ydeng@lzb.ac.cn (Y. Deng).



Scheme 1. (A) Synthesis of BHDC from HDA and BC; (B) and (C) two side reactions.

[22], here the non-phosgene yielding of HDC, in particular the synthesis of dibutyl hexamethylenedicarbamate (BHDC) from 1,6-hexamethylenediamine (HDA) and BC in *n*-butanol, were efficiently catalyzed over $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, etc. (Scheme 1A). The effects of varied reaction conditions, i.e., reaction temperature, reaction time, molar ratio of reactants, catalyst content, etc. on the catalytic activity were also investigated in detail.

2. Experimental

2.1. Chemicals and catalysts

All chemicals used in the experiments were of analytical grade, and were used without further purification otherwise specified. MC, EC and BC with 98–99% purity were synthesized in our laboratory. $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ employed as catalyst were also analytical grade and used as received. Additionally, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was pretreated with HDA, BC and *n*-butanol at 473 K for 1 h, respectively.

2.2. Reaction procedure

All reactions were conducted in a 120 mL stainless autoclave equipped with magnetic stirring. In each reaction, HDA (7.5 mmol), alkyl carbamates (15–45 mmol), corresponding alcohol (37.5–187.5 mmol), and a catalyst (17–52 mg) were charged successively into the autoclave flushed with N_2 gas. The reaction proceeded from 433 to 473 K for 1–6 h. After reaction and the autoclave cooled to room temperature, the catalyst and insoluble compound were separated from the resulted reaction mixture by

centrifugation and filtration. About 95% of the catalyst could be recovered and was reused for the next time with additional fresh catalyst in ca. 5% of total amount charged. After alcohol in the filtrate was distilled, 100 mL water was added, then, the desired white solid product could be obtained by precipitation. The isolated yields of products were expressed based on the amount HDA charged.

2.3. Identification

The products were qualitatively and quantitatively analyzed with GC–MS (HP 6890/5973), ^1H NMR (Bruker AMX FT 400-MHz), elemental analysis (Elementar Analysensysteme GmbH VarioEL using the software Version V 3.00), and HP 6820 GC equipped with a FID detector using biphenyl as an internal standard. IR analysis was conducted with a Thermo Nicolet 5700 FT-IR spectrometer. X-ray diffraction (XRD) was measured on a Siemens D/max-RB powder X-ray diffract meter. Diffraction patterns were recorded with Cu $\text{K}\alpha$ radiation (30 mA, 40 kV) over a 2θ range of 10° to 50° and a position-sensitive detector using a step size of 0.017° . X-ray photoelectron spectroscopy (XPS) analysis was performed with a VG ESCALAB 210 instrument. Mg $\text{K}\alpha$ radiation at a pass energy of 150 eV at an energy scale calibrated versus C1s peak at 285.00 eV arising from adventitious carbon were used.

3. Results and discussion

3.1. Effects of different catalysts

Firstly, for the purpose of comparison, a blank experiment for synthesizing BHDC from HDA and BC in *n*-butanol was conducted (Table 1, entry 1), and the results showed that only 5% yield of BHDC

Table 1
Effects of different catalysts on the synthesis of HDC^a.

Entry	Catalyst	Carbonyl source	Conversion (%) ^b	Product yield (%) ^c	Byproduct yield (%)		TON ^d
					Polyurea ^c	Dialkyl carbonate	
1	No Cat.	BC	33	5	90	1.2	–
2	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	BC	55	27	65	1.9	83
3	$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	BC	60	56	39	4.5	102
4	$\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	BC	62	61	32	5.4	104
5	$\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$	BC	67	80	13	8.5	173
6	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	BC	54	27	66	1.6	159
7	$\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$	BC	56	28	64	2.2	164
8	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	BC	68	85	10	10.1	178
9 ^e	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	BC	64	82	12	10.5	167
10	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	MC	51	34	59	3.5	133
11	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	EC	63	81	14	6.1	165

^a Reaction conditions: HDA, 7.5 mmol; alkyl carbamate, 30 mmol; alcohol, 112.5 mmol; Cat., 44 mg; reaction temperature, 453 K; reaction time, 5 h. The conversion of HDA was nearly 100% in all entries.

^b Conversion of alkyl carbamate.

^c Isolated yield based on HDA charged.

^d TON, mole of alkyl carbamate converted per mole of catalyst.

^e Reused for the fourth time.

could be obtained, although HDA conversion was nearly 100%. This result suggested that HDA was easy to react in the presence of BC, although most products were the undesirable byproduct. Among them, the main byproduct was a sort of amorphous solid compound (ca. 90% yield), which was insoluble in the usual solvents (e.g., ethanol, acetone, DMF, etc.) and could be separated from the reaction system by filtration. After drying, FT-IR spectrum was used to confirm its identity, and a peak at 1616 cm^{-1} could be observed, which could be attributed to the carbonyl group of polyurea compounds [23]. Thus, we deduced that this amorphous solid byproduct should be a polyurea compound from the polycondensation of HDA and BC. Besides polyurea byproduct, ca. 1.2% $\text{C}_4\text{H}_9\text{OC(O)OC}_4\text{H}_9$ (DBC) from the side reaction (Scheme 1B) and trace $\text{C}_4\text{H}_9\text{NHC(O)OC}_4\text{H}_9$ (N-BBC) from another side reaction (Scheme 1C) could be observed by gas chromatography and GC-MS analysis in the blank experiment. Surprisingly, no butyl-6-aminohexane-1-carbamate was detected in the byproducts.

Secondly, the catalytic activities of seven catalysts were investigated, respectively. Under the same conditions as the blank experiment, i.e., the reaction was operated at 453 K for 5 h, molar ratio of *n*-butanol to BC to HDA was 15:4:1, and the catalyst content was 5 wt.% (based on the weight of HDA), the catalytic results were listed in Table 1 (entries 2–8). It can be seen that, 27–85% BHDC yields were obtained with the BC conversions of 54–68% and the TON of 83–178, indicating that all the nitrate and acetate catalysts employed in this work exhibited moderate to high catalytic activities. Among them, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ exhibited the highest activity, i.e., yielding 85% BHDC when 68% BC was consumed, meanwhile, the TON of 178 was obtained and only 10% polyurea byproduct was yielded. $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ was also capable of catalyzing the reaction efficiently, but the efficiency seems to be slightly inferior as compared with that of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. That is, a 80% BHDC yield with a 67% BC conversion and a 173 TON could be obtained in the presence of $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, while 13% polyurea byproduct was formed. For $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ catalysts, only 27–28% BHDC yields but 64–66% polyurea byproduct could be obtained, although their TONs were also more than 80, indicating that these catalysts were not suitable for this catalytic reaction.

Moreover, the recycling of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ catalyst was also examined (Table 1, entry 9). When the catalyst was reused for the fourth time, a 82% BHDC yield could still be achieved with a 64% BC conversion and a TON of 167, meanwhile only 12% polyurea byproduct was formed, showing that the $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ catalyst possessed good recyclability. In order to investigate the universality of the catalyst, the syntheses of dimethyl hexamethylenedicarbamate (MHDC) and diethyl hexamethylenedicarbamate (EHDC) using MC and EC as substrates were also conducted over $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Table 1, entries 10 and 11). As the results showed, under the same conditions, high activity of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for synthesis of EHDC could also be exhibited with a 81% EHDC yield, a TON of 165, and only 14% polyurea byproduct. However, poor results of 34% MHDC yield but 59% polyurea byproduct could be obtained for synthesis of MHDC with a 51% BC conversion and a TON of 133. This means that the $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ catalyst is more suitable for synthesis of BHDC than MHDC and EHDC.

3.2. Effects of reaction temperature and reaction time

The effects of reaction temperature on the synthesis of BHDC were shown in Fig. 1. It can be seen that, with the temperature increasing from 433 to 453 K, BHDC yield increased from 7 to 85%, while the isolated yield of main byproduct polyurea decreased from 86 to 10%, indicating that the formation of polyurea was easier at low temperature while the high temperature favored the synthesis of BHDC. This trend was in accordance with that

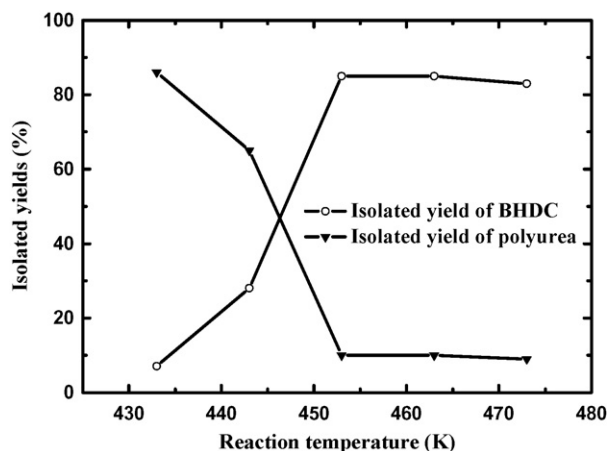


Fig. 1. Effects of reaction temperature on the synthesis of BHDC: HDA, 7.5 mmol; BC, 30 mmol; $\text{C}_4\text{H}_9\text{OH}$, 112.5 mmol; $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 44 mg; reaction time, 5 h.

reported in previous studies [24]. When the temperature further increased from 463 to 473 K, the BHDC yield showed a slight decrease (i.e., from 85 to 83%), which might be caused by the partial thermal decomposition of BHDC at higher temperatures.

Fig. 2 showed the effects of reaction time on the yields of BHDC and the byproduct polyurea. From the curves, it can be seen that the yield of BHDC was 7% in the first hour. But then, it increased suddenly to 76% while the yield of polyurea decreased sharply from 85 to 17% in a narrow time range from 1 to 2 h. With the reaction time increased unceasingly, the BHDC yield increased smoothly to 85% at 5 h while polyurea decreased to 10%. When the reaction time was further prolonged to 6 h, a slightly decrease in BHDC yield (84%) was obtained. From the above discussion, it can be conjectured that a pre-activation of the catalyst might occur at the initial stage of this reaction. A similar phenomenon has also been observed in previous literature [25], which was called as an induction period by the author. More discussions about this would be stated in Section 3.4.

3.3. Effects of molar ratio of BC/HDA, *n*-butanol/HDA, and the amount of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

The effects of molar ratio of BC/HDA on the catalytic reaction were shown in Fig. 3. With increasing the molar ratio of BC/HDA from 2:1 to 4:1, the BHDC yield also increased from 34 to 85%

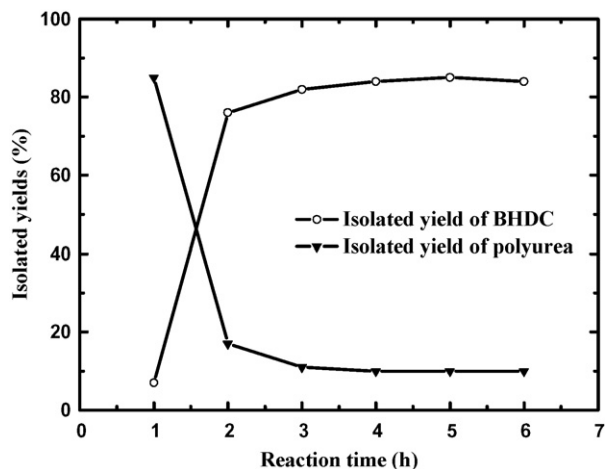


Fig. 2. Effects of reaction time on the synthesis of BHDC: HDA, 7.5 mmol; BC, 30 mmol; $\text{C}_4\text{H}_9\text{OH}$, 112.5 mmol; $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 44 mg; reaction temperature, 453 K.

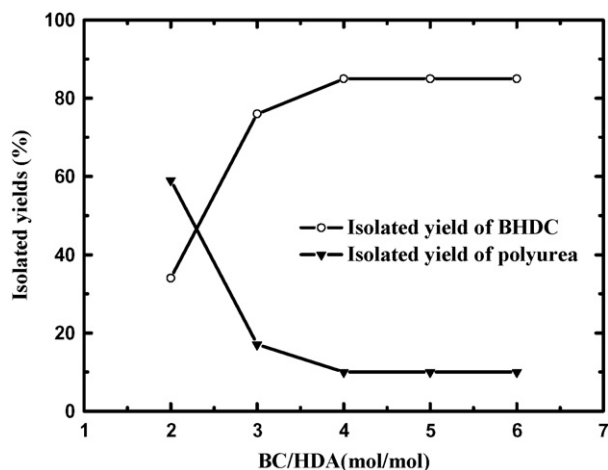


Fig. 3. Effects of molar ratio of BC/HDA on the synthesis of BHDC: HDA, 7.5 mmol; C_4H_9OH , 112.5 mmol; $Y(NO_3)_3 \cdot 6H_2O$, 44 mg; reaction temperature, 453 K; reaction time, 5 h.

while the byproduct polyurea yield decreased from 59 to 10%, indicating that excessive BC would facilitate the production of BHDC. This might be explained by the fact that part BC was consumed to yield byproducts (e.g., DBC and N-BBC) during reaction. When the ratio was higher than 4:1, no obvious changes in BHDC yield were observed, suggesting that the optimum BC/HDA ratio should be 4:1.

Fig. 4 displayed the effects of the amount of *n*-butanol on the reaction. With increasing the mole ratio of *n*-butanol/HDA from 5:1 to 15:1, the BHDC yield increased from 72 to 85%, while byproduct polyurea yield decreased from 21 to 10%. When the amount of *n*-butanol employed in the reaction was further increased, an obvious decrease in the BHDC yield and the yielding of more byproduct polyurea could be obtained, i.e., the BHDC yield decreased from 85% at the *n*-butanol/HDA ratio of 15:1 to 75% at the *n*-butanol/HDA ratio of 25:1, and the polyurea yield increased from 10 to 17% accordingly. It might be because the reactants would disperse and react effectively in an appropriate amount of *n*-butanol, however, if reactants were further diluted by a large amount of excessive *n*-butanol, the reaction rate would be slowed down, thus resulting in the decline of BHDC yield.

The effects of the amount of $Y(NO_3)_3 \cdot 6H_2O$ catalyst on the yield of BHDC was examined at 453 K using a *n*-butanol/BC/HDA molar

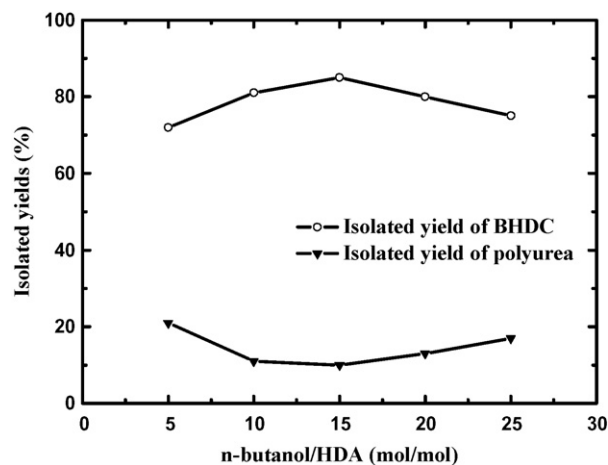


Fig. 4. Effects of molar ratio of *n*-butanol/HDA on the synthesis of BHDC: HDA, 7.5 mmol; BC, 30 mmol; $Y(NO_3)_3 \cdot 6H_2O$, 44 mg; reaction temperature, 453 K; reaction time, 5 h.

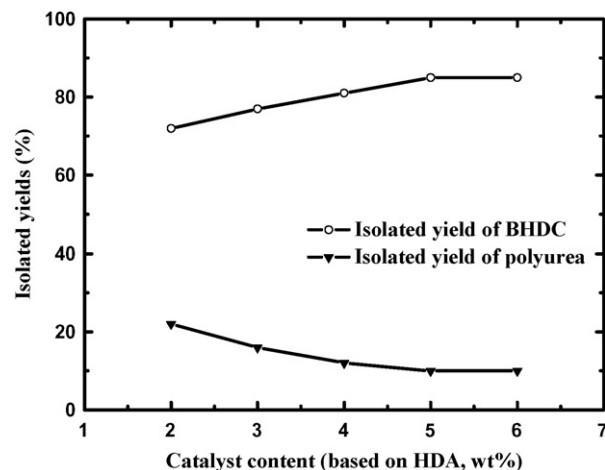


Fig. 5. Effects of catalyst content on the synthesis of BHDC: HDA, 7.5 mmol; BC, 30 mmol; C_4H_9OH , 112.5 mmol; reaction temperature, 453 K; reaction time, 5 h.

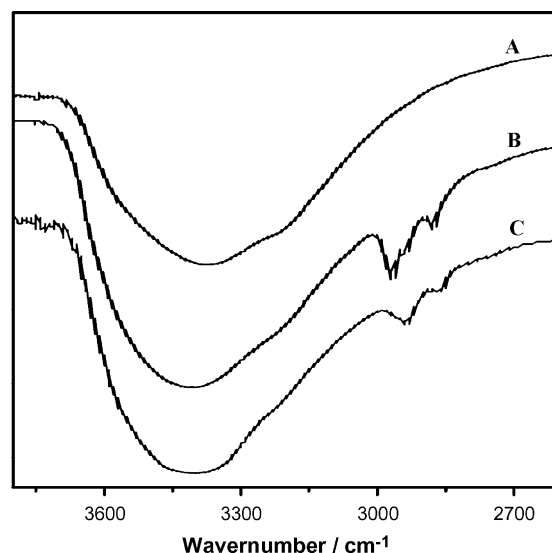


Fig. 6. FT-IR spectra of $Y(NO_3)_3 \cdot 6H_2O$ samples: (A) fresh, (B) pretreated with *n*-butanol, and (C) used.

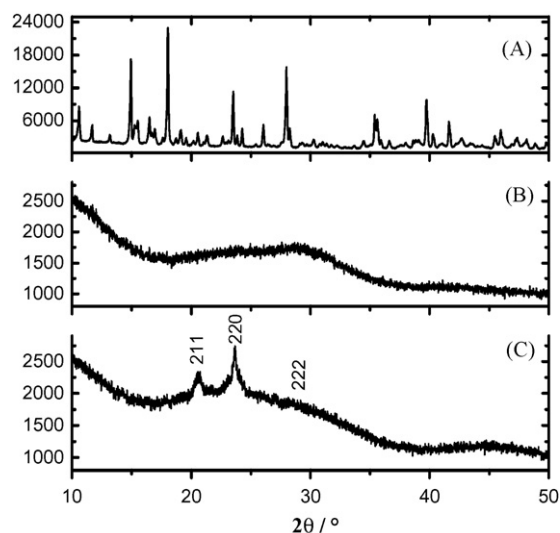


Fig. 7. XRD patterns of $Y(NO_3)_3 \cdot 6H_2O$ samples: (A) fresh, (B) pretreated with *n*-butanol, and (C) used.

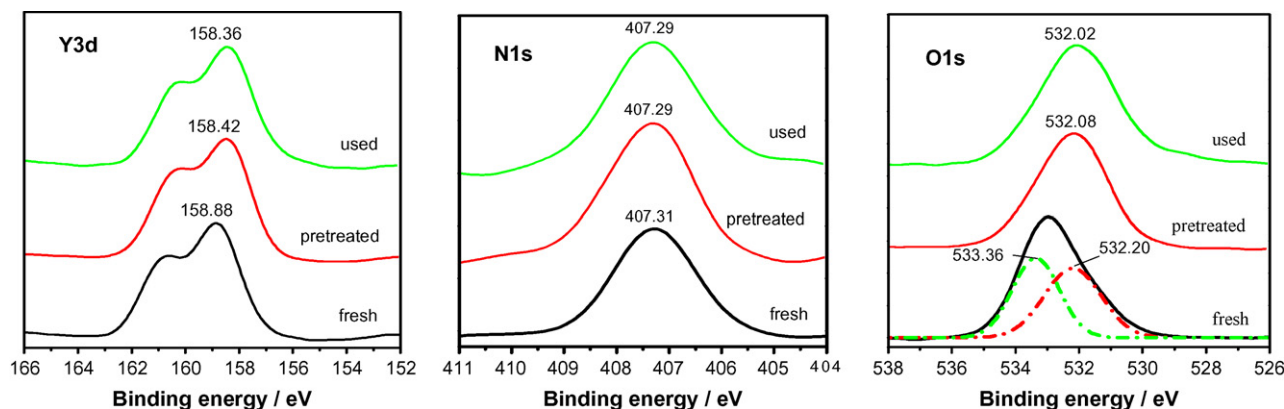


Fig. 8. XPS spectra of Y3d, N1s and O1s core level electrons of fresh, pretreated and used $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

ratio of 15:4:1. The results in Fig. 5 showed that, the yields of BHDC were improved with increasing the amount of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, i.e., from 72% yield at the catalyst amount of 2 wt.% (based on the weight of HDA) to a maximum of 85% yield at the catalyst amount of 5 wt.%. With further increasing the amount of catalyst, the yield would not change obviously. Contrary to the BHDC, the yield of byproduct polyurea decreased with increasing the amount of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, that is, the yield firstly decreasing from 22% at 2 wt.% catalyst amount to a minimum of 10% at 5 wt.% catalyst amount, and thereafter, the values keeping relatively constant. Therefore, the optimum content of catalyst was chosen as 5 wt.%.

3.4. The pre-activation and characterizations of the catalysts

As shown in Fig. 2, a clear induction phenomenon was observed in this reaction. For further study, the $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was firstly pretreated with HDA, BC and *n*-butanol at 473 K for 1 h, respectively. After that, the pretreated $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was employed in synthesis of BHDC at 453 K for 1 h. The results showed that the BHDC yields were only 8 and 3% when $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were pretreated with HDA and BC, respectively. However, when the catalyst was pretreated with *n*-butanol, the BHDC yield rapidly increased to 60% in 1 h. Comparing with the result of only 3–8% BHDC yield in 1 h when $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was not pretreated or pretreated with HDA and BC, respectively, the pretreatment of catalyst with *n*-butanol remarkably improved the catalytic activity of the catalyst, indicating that *n*-butanol take part in the transformation of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ into some catalytically active species.

With the aim of finding out how *n*-butanol acted actually on the catalyst during pretreatment, FT-IR, XRD and XPS were used to investigate the changes of fresh, pretreated with *n*-butanol and used $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ catalysts. Each sample was dried at 393 K for 3 h in vacuum before characterizations. As FT-IR spectra showed (Fig. 6), the pretreated catalyst displayed additional absorbance bands near 2900 cm^{-1} compared with the fresh sample, which should be ascribed to the stretching vibrations of aliphatic C–H. These peaks were also observed in FT-IR spectra of the used catalyst, proving that some interactions occurred between the catalyst and *n*-butanol.

X-ray diffraction patterns were illustrated in Fig. 7, and the $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ without any pretreatment showed characteristic diffraction peaks. After pretreatment, these peaks disappeared, while an amorphous phase displayed. The XRD pattern of used catalyst was also similar to that of the pretreated catalyst, except several new diffraction peaks at 20.65° , 23.66° and 29.13° , corresponding to the *d*-spacing of 4.30, 3.76 and 3.07 \AA , which assigned to the (2 1 1), (2 2 0) and (2 2 2) facets of Y_2O_3 . This revealed the catalyst altered

from crystal into amorphous matters and some Y_2O_3 formed during the reaction.

Fig. 8 gave the XPS spectra of Y3d, O1s and N1s. Comparing the binding energy (BE) of fresh catalyst with that of pretreated catalyst, the BE of $\text{Y}3d_{5/2}$ decreased from 158.88 eV, but the BE of N1s was almost not changed (i.e., 407.31 eV for the fresh catalyst and 407.29 eV for the pretreated catalyst). For the O1s emissions, the corresponding BE of O in NO_3^- changed slightly from 532.20 to 532.08 eV, while the peak of O in crystal H_2O of fresh catalyst (533.36 eV) became unobvious after pretreatment. For the pretreated catalyst and the used catalyst, almost the same BE values were observed (i.e., 158.36 eV of $\text{Y}3d_{5/2}$, 407.29 eV of N1s, and 532.02 eV of O1s for the used catalyst). The changes of catalyst atomic ratio in surface layer were also estimated. For fresh catalyst, the ratio of N/Y and O/Y was 1.0 and 4.1, and after pretreatment, the ratio declined to 0.1 and 2.9, indicating that part NO_3^- decompose. Through comparing the used catalyst with the pretreated one, only a little changes in the atomic ratio of N/Y and O/Y could be obtained (i.e., N/Y = 0.2 and O/Y = 2.6 for the used catalyst, and the values were 0.1 and 2.9 for the pretreated catalyst, respectively), suggesting that the composition of the catalyst after being pretreated was relatively steady.

Based on the above characterizations, we deduced that the catalyst should undergo an induction period during the reaction. The high activity of pretreated catalyst with *n*-butanol not only verified this point, but also proved that *n*-butanol took part in the pre-activation of the catalyst. During reaction or the pretreatment, some transformations for the catalyst, i.e., part decomposition of $\text{Y}(\text{NO}_3)_3$ to Y_2O_3 , conversion from crystal to amorphous state, changing in chemical state of the active species, as well as some subtle interactions between the catalyst and *n*-butanol, occurred and all of these changes might be the reason resulting in the activation of the catalyst.

4. Conclusions

In summary, the non-phosgene synthesis of HDC, in particular the synthesis of BHDC from HDA and BC in *n*-butanol, were successfully carried out. In the presence of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and in *n*-butanol at 453 K for 5 h, nearly 100% HDA conversion and a 85% BHDC isolated yield could be achieved with a TON of 178. Under the same conditions, the yields of MHDC and EHDC were 34 and 81%, respectively. The effects of varied catalysts and different reaction conditions were also investigated in detail, and the optimized conditions were as follows: the reaction temperature and time was 453 K and 5 h, the molar ratio of *n*-butanol/BC/HDA was 15:4:1, and the amount of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ catalyst was 5 wt.% (based on the

weight of HDA). During reaction, an induction period was observed, which was also verified by the high activity of pretreated catalyst. FT-IR, XRD, XPS analysis and comparisons of fresh, pretreated and used catalysts revealed that some transformation for the catalyst occurred during reaction or the pretreatment, and *n*-butanol took part in the activation of the catalyst. Further investigations are under way.

References

- [1] O. Bayer, *Angew. Chem.* 59 (1947) 257–272.
- [2] C.S. Schollenberger, US 2,871,218 (1959).
- [3] P.A. Tierney, R.M. Hedrick, J.D. Gabbert, US 3,833,534 (1974).
- [4] D.J. Goldwasser, R.W. Oertel, US 4,567,236 (1986).
- [5] (a) K. Sato, *Hydrocarbon Proces.* 45 (1966) 177–179;
(b) H.J. Twichett, *Chem. Soc. Rev.* 3 (1974) 209–230.
- [6] (a) W.D. Mcghee, T.E. Waldman, US 5,298,651 (1994);
(b) T.E. Waldman, W.D. Mcghee, *J. Chem. Soc., Chem. Commun.* (1994) 957–958.
- [7] S. Braverman, M. Cherkinsky, L. Kedrova, A. Reisman, *Tetrahed. Lett.* 40 (1999) 3235–3238.
- [8] (a) J.E. Lyons, US 3,960,914 (1976).;
(b) V.N.M. Rao, G.E. Heinsohn, US 4,537,726 (1985).;
(c) J.A. Sofranko, A.M. Gaffney, US 5,126,480 (1992).
- [9] A. Brändström, B. Lamm, I. Palmertz, *Acta Chem. Scand.* 28B (1974) 699–701.
- [10] R. Tsumura, U. Takiki, T. Abe, US 4,081,472 (1978).
- [11] V.L.K. Valli, H. Alper, *J. Org. Chem.* 60 (1995) 257–258.
- [12] M. Franco, C. Carlo, EP 0 492 556 A1 (1992).
- [13] R. Sundermann, K. König, T. Engbert, G. Becker, G. Hammen, US 4,388,246 (1983).
- [14] W.D. Mcghee, D.P. Riley, *Organometallics* 11 (1992) 900–907.
- [15] (a) J.S. Lee, C.W. Lee, S.M. Lee, K.H. Park, *J. Mol. Catal.* 61 (1990) L15–L18;
(b) V.L.K. Valli, H. Alper, *Organometallics* 14 (1995) 80–82.
- [16] W. Mcghee, D. Riley, K. Christ, Y. Pan, B. Parnas, *J. Org. Chem.* 60 (1995) 2820–2830.
- [17] (a) M. Distaso, E. Quaranta, *Appl. Catal. B* 66 (2006) 72–80;
(b) I. Vauthey, F. Valot, C. Gozzi, F. Fache, M. Lemaire, *Tetrahed. Lett.* 41 (2000) 6347–6350;
(c) Z.H. Fu, Y. Ono, *J. Mol. Catal.* 91 (1994) 399–405;
(d) B. Hans-Josef, K. Heinrich, R. Wolfgang, EP 0 048 371 (1982);
(e) M. Aresta, A. Dibenedetto, E. Quaranta, M. Boscolo, R. Larsson, *J. Mol. Catal. A* 174 (2001) 7–13.
- [18] H. Peter, K. Klaus, F. Rudolf, F. Kurt, DE 2 943 480 A1 (1981).
- [19] Q. Li, J. Wang, W. Dong, M. Kang, X. Wang, Sh. Peng, *J. Mol. Catal. A* 212 (2004) 99–105.
- [20] G. Laqua, U. Schoner, A. Otterbach, H.V. Schwarz, WO 9,717,323 (1997).
- [21] F. Merger, F. Towae, US 4,497,963 (1985).
- [22] (a) T. Sima, S. Guo, F. Shi, Y. Deng, *Tetrahed. Lett.* 43 (2002) 8145–8147;
(b) F. Shi, Y. He, D. Li, Y. Ma, Q. Zhang, Y. Deng, *J. Mol. Catal. A* 244 (2006) 64–67;
(c) H. Zhou, F. Shi, X. Tian, Q. Zhang, Y. Deng, *J. Mol. Catal. A* 271 (2007) 89–92;
(d) F. Shi, Y. Deng, T. SiMa, H. Yang, *J. Catal.* 203 (2001) 525–528;
(e) F. Shi, Y. Deng, T. SiMa, J. Peng, Y. Gu, B. Qiao, *Angew. Chem. Int. Ed.* 42 (2003) 3257–3260.
- [23] R.G. Deleon, A. Kobayashi, T. Yamauchi, J. Ooishi, T. Baba, M. Sasaki, F. Hiarata, *Appl. Catal. A* 225 (2002) 43–49.
- [24] F. Merger, F. Towae, US 4,713,476 (1987).
- [25] T. Baba, A. Kobayashi, Y. Kawanami, K. Inazu, A. Ishikawa, T. Echizenn, K. Murai, S. Asoc, M. Inomata, *Green Chem.* 7 (2005) 159–165.