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Preparation of 1,4-cyclohexanedimethanol by selective hydrogenation of a waste PET monomer bis(2-hydroxyethylene terephthalate)

Xiaonan Guo,^{ab} Jiayu Xin,^b Xingmei Lu,^b Baozeng Ren^{*a} and Suojiang Zhang^{*b}

A new approach is developed for the preparation of 1,4-cyclohexanedimethanol (CHDM) by hydrogenation of bis(2-hydroxyethylene terephthalate) (BHET) obtained from waste poly(ethylene terephthalate) (PET). The influences of various reaction parameters including temperature, pressure and time, on the hydrogenation reaction were studied, and the 100% conversion of BHET and 78% yield of CHDM were achieved with Pd/C and Cu-based catalysts. X-ray diffraction, low temperature N₂ adsorption-desorption and H₂ temperature-programmed reduction were used to characterize the Cu-based catalysts, demonstrating that the Cu⁺/Cu⁰ species are the active sites. This study not only provides a new route for the production of CHDM, but also an approach for the efficient utilization of waste PET.

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1. Introduction

1,4-Cyclohexanedimethanol (CHDM) is a highly valued and extensively used chemical in the polymer industry. It is used in paints and particularly as a modified material for fibers and polyesters1 such as poly(ethylene terephthalate-co-1,4-cylclohexylenedimethylene terephthalate) (PETG) with excellent performance such as thermal resistance, weather resistance and physical strength.² Due to the wide application of the high performance polyesters, the demand of CHDM will be increasing significantly. Industrially, CHDM is prepared by a two-step process using two reactors. The first step is the highly exothermic conversion of dimethyl terephthalate (DMT) into dimethyl hexahydroterephthalate (DMHT) by the hydrogenation of the phenyl group using catalysts including Ni, Pd, Ru, Rh, added Pt, Ba, Ca and other additives in the temperature range of 433-453 K and an H₂ pressure of 5-48 MPa.³⁻⁷ The second step is the conversion of DMHT into CHDM by the hydrogenation of the ester groups to hydroxyl groups using conventional Cu-based catalysts^{8,9} such as Cu-Cr or Cu-Zn catalysts,¹⁰ added Mn, Ba and other catalysts containing Ru¹¹⁻¹³ and Fe-based catalysts bearing a PNP-pincer ligand¹⁴ in the temperature range of 473-573 K and the reaction pressure of 3-15 MPa.

There are some studies on the preparation of CHDM by other means. A new process for producing CHDM by the hydrogenation of terephthalic acid (TPA) into 1,4-cyclohexanedicarboxylic acid (CHDA) using Pd- or Ru-based catalysts, and further getting CHDM from CHDA¹⁵ was described. Recently, Thomas and coworkers reported that bimetallic nanoparticle catalysts,¹⁶ such as silica-supported Ru₅Pt, Ru₁₀Pt₂, Ru₆Pd₆, Ru₁₂Cu₄ and a trimetallic cluster Ru₅PtSn¹⁷ can promote the single-step conversion of DMT into CHDM under mild reaction conditions.¹⁸ However, both the conversion and selectivity are not so satisfactory.

However, the above raw materials are derived from petroleum industries and the hydrogenation processes are carried out in solvents such as ethyl acetate, tetrahydrofuran and methanol, which increase the difficulty in the separation of products and the cost of the process. Therefore, it is imperative to find a low-cost material and a solvent-free process for the synthesis of CHDM.

Herein, we developed a new solvent-free route to produce CHDM using the waste poly(ethylene terephthalate) (PET) derived monomer bis(2-hydroxyethylene terephthalate) (BHET) as the raw material. The low-cost material and the solvent-free process can reduce the cost and simplify the process significantly. BHET can be easily obtained from the glycolysis of waste PET, which was carried out conventionally in ethylene glycol solution under 393-463 K, 1-5 h and atmospheric pressure using various kinds of catalysts such as zinc acetate, cobalt acetate19-22 and ionic liquids.23-25 BHET has a potential for the conversion into chemicals of utility, which can be used as the raw material to synthesize the fatty amide derivatives,26 unsaturated polyester resin²⁷ and hydrophobic textile dyestuffs.²⁸ However, there are still few studies on the application of BHET. Therefore, transforming BHET easily obtained from waste PET into high value-added CHDM is of great significance, which contributes to the recycling of resources.

In this paper, it is found that BHET obtained from waste PET can be efficiently converted to CHDM as shown in Scheme 1,

[&]quot;School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou, Henan, 450001, P. R. China. E-mail: renbz@zzu.edu.cn

^bBeijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: sjzhang@home.ipe.ac.cn





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which has not been reported to date. It was carried out by a twostep process using the traditional catalyst Pd/C and Cu-based catalysts. In the first step, the phenyl group was selectively hydrogenated to cyclohexane catalyzed by Pd/C catalyst. In the second step, the ester groups were selectively hydrogenated to hydroxyl groups catalyzed by Cu-based catalysts. The aim of this paper is to provide a new method that can selectively hydrogenate BHET to CHDM. The influences of various reaction parameters, including reaction temperature, pressure and time, on the two hydrogenate reactions were investigated to get the optimal reaction conditions. Moreover, X-ray diffraction, low temperature N_2 adsorption–desorption and H_2 temperatureprogrammed reduction were used to characterize the Cubased catalysts.

2. Experimental

2.1. Materials

BHET (\geq 99%) was obtained by the degradation of the waste PET in our laboratory. Copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, \geq 99%) and chromium(III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, \geq 99%) were obtained from Sinopharm Chemical Reagent Co., Ltd, China. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, \geq 99%), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, \geq 99%), and sodium carbonate (Na₂CO₃, \geq 99%) were obtained from Xilong Chemical Co., Ltd, China. 10% Pd/C was obtained from J & K Scientific Ltd, China. The materials were used without any further treatment.

2.2. Preparation of Cu-based catalysts

2.2.1. Preparation of Cu–Cr catalyst. The Cu–Cr catalyst was prepared by a conventional co-precipitation method.²⁹ In a typical synthesis, $Cu(NO_3)_2 \cdot 3H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ with a desired molar ratio (Cu : Cr = 1 : 1) were dissolved in 50 mL deionized water at 333 K with stirring, the solution was

precipitated by adding sodium carbonate until the pH of the solution reached 8. The precipitate was aged at 333 K for 3 h and then filtered and washed several times with deionized water. The obtained solid sample was dried at 393 K for 12 h in an oven and then calcined at 723 K for 4 h to provide the as-prepared oxide. The as-prepared oxide was reduced by 5% H₂ in Ar at the programmed temperature which is rising from room temperature to 493 K staying 1 h by the rate of 4 K min⁻¹, then to 623 K staying 2 h by the rate of 1 K min⁻¹ to obtain the final Cu–Cr catalyst.

2.2.2. Preparation of Cu–Zn/Al₂O₃ catalyst. Firstly, an aqueous solution was prepared with $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with molar ratio of $Cu^{2+} : Zn^{2+} : Al^{3+} = 5 : 4 : 1,^{30}$ then the solution was precipitated by adding sodium carbonate until the pH of the solution reached 7 at 333 K with stirring. The precipitate was aged at 333 K for 3 h and then filtered and washed several times by deionized water. The obtained solid sample was dried at 393 K for 12 h in an oven and then calcined at 723 K for 4 h to provide the asprepared oxide. The as-prepared oxide was reduced by H₂ under 573 K before use.

2.3. Hydrogenation reaction of BHET to CHDM

All hydrogenation reactions were carried out in a 100 mL stainless steel high pressure reactor (MSC County Petroleum Research Instruments, Jiangsu, China), equipped with magnetic stirring. The hydrogenation reaction of BHET to CHDM was carried out by a two-step process as shown in Scheme 2. In the first step, the reactor was charged with 2.0 g of BHET as starting material and 0.1 g of 10% Pd/C catalyst.³¹ The reactor was then purged with H₂ three times to remove air and then pressurized to the desired pressure of H₂ and heated to the desired temperature under stirring of 400 rpm. After the reaction, the intermediate products which are mainly consisted of bis(2-hydroxyethyl) cyclohexane-1,4-dicarboxylate (BHCD) was



Scheme 2 The two-step process for the hydrogenation of BHET to CHDM without solvent.

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2.4. Characterization and analysis

The structures and crystal phase compositions of the Cu–Cr and Cu–Zn/Al₂O₃ catalysts were determined by Powder X-ray diffraction (XRD) patterns with a Bruker D8-Advance X-ray powder diffractometer using Cu K α radiation within a 2 θ range of 5–85° in steps of 10°, operated at an accelerating voltage of 40 kV and an emission current of 200 mA.

Temperature-programmed reduction (TPR) of the Cu-based catalysts was carried out in a stream of 90% Ar and 10% H_2 with a flowing rate of 50 mL min⁻¹, and the samples were heated at 10 K min⁻¹ from room temperature to 773 K.

The intermediate products of the first step were analyzed by HPLC (Agilent 1100) fitted with a refractive index detector and an ODS-BP column (0.46 mm \times 250 mm). The mixture of acetonitrile and water with a ratio of 1 : 1 was used as mobile phase. The oven temperature for the determination of standards and samples was set at 313 K with a flow rate of 0.5 mL min⁻¹. The final products from the second step were analyzed by gas chromatography on a GC-2014 instrument (Shimadzu Corporation) equipped with a HP-5 chromatographic column and a flame ionization detector (FID). The products were identified by GC (Agilent 6890N)-MS (Agilent 5975B) equipped with a HP-5ms UI chromatographic column. The conversion and yield of products were calculated by eqn (1) and (2) as follows:

$$Conversion(\%) = \left(1 - \frac{\text{moles of unreacted reactant}}{\text{moles of reactant}}\right) \times 100$$
(1)

$$Yield(\%) = \frac{moles of certain product}{moles of reactant} \times 100$$
 (2)

3. Results and discussion

3.1. Hydrogenation of BHET to BHCD

In the first step, BHET was converted to BHCD by the selective hydrogenation of phenyl group to cyclohexane group, which was performed on 10% Pd/C catalyst without solvent. In order to get the maximum direction of the main reaction, we investigated the influences of different reaction conditions on the reaction to get the optimal reaction conditions. Moreover, we report the possible reaction pathway for the hydrogenation of BHET to BHCD as shown in Scheme 3.

3.1.1. Influence of reaction temperature. The influence of reaction temperature on the conversion of BHET and yields of BHCD and main by-products is shown in Fig. 1. It displays that the reaction temperature is particularly important for the hydrogenation reaction. The conversion of BHET increased and



Scheme 3 The possible reaction pathway for the hydrogenation of BHET to BHCD.

reached almost 100% when the reaction temperature reached 428 K. The yield of BHCD initially increased and then decreased with the increase of the reaction temperature.

Because the further increase of the temperature, the reaction shifted to side pathways including the hydrogenation of the ester and hydroxyl groups of BHET which is confirmed by the appearance of the by-products 4 and 5, and the excessive hydrogenation of the ester and hydroxyl groups of BHCD which is confirmed by the appearance of the by-products 1, 2, 3 and 6. The yields of by-products 3 and 5 increased while the yields of by-products 1, 2, and 4 decreased with the increase of the reaction temperature. The by-product 6 occurred when the temperature was above 498 K, which indicates that the further



Fig. 1 Influence of reaction temperature on the conversion of BHET and yields of BHCD and main by-products. Reaction conditions: 2.0 g BHET, 0.1 g 10% Pd/C, 3.5 MPa, and 5 h.

hydrogenation becomes easy at high temperature. It can be concluded that 428 K is the optimal reaction temperature for the hydrogenation of BHET to BHCD.

3.1.2. Influence of reaction time. Fig. 2 presents the influence of reaction time on the conversion of BHET and yields of BHCD and main by-products. It is shown that the conversion of BHET increased with the increase of the reaction time. However, the yield of the BHCD increased rapidly in reaction time before 3 h but decreased slightly with the further increase of the reaction time, which implies that the further hydrogenation of BHCD leads to more side reactions. The yield of the by-product 1 increased, while the yield of the by-product 2 increased initially and then decreased with the increase of the reaction time. Moreover, the by-products 3 and 4 occurred when the reaction time was longer than 4 h, indicating that the terminal hydroxyl group is easier to be reduced than the ester group catalyzed by Pd/C, and the further increase of the reaction time would not only reduce the yield of the main product but also not distinctly affect the conversion. Based on the analysis, a reaction time of 3 h gave the highest product yield and lowest side products and therefore it is regarded as the best reaction time.

3.1.3. Influence of reaction pressure. Fig. 3 shows the influence of reaction pressure on the conversion of BHET and yields of BHCD and main by-products. It is observed that with an increase of the reaction pressure, the conversion of BHET increased and the yield of the BHCD increased and the rate of the increase in the yield of BHCD became smaller. The byproducts 5 and 6 disappeared when the reaction pressure was above 5.5 MPa. The by-products 1 and 2 increased and then decreased with the increase of the reaction pressure. However, the by-products 3 and 4 were not detected in the products. It indicates that the high pressure improves the selectivity of the hydrogenation of phenyl to cyclohexane, but could not remove the further hydrogenation of ester and hydroxyl groups. It can be concluded that a certain range under 7 MPa of the high pressure can not only drive the equilibrium to move to the desired direction but also prevent the catalysts from losing activity.



Time (h)

- Conversion

- BHCD



Fig. 3 Influence of reaction pressure on the conversion of BHET and yields of BHCD and main by-products. Reaction conditions: 2.0 g BHET, 0.1 g 10% Pd/C, 2 h, and 428 K.

3.1.4. Influence of stirring rate. Fig. 4 shows the influence of stirring rate on the conversion of BHET and the yield of BHCD. As can be seen, the conversion of BHET and yield of BHCD firstly increased with the increase of the stirring rate from 50 to 300 rpm, and then kept stable from 300 to 600 rpm. Thus, there should be no mass or heat transfer limitation with a stirring rate higher than 300 rpm.

As a consequence, the Pd/C catalyst shows high activity and selectivity of the hydrogenation of BHET to BHCD without solvent under respective mild reaction conditions. Under the optimal reaction conditions of 428 K, 3 h, and 7 MPa, the conversion of BHET and the yield of BHCD have reached 100% and 95%, respectively.

3.2. Hydrogenation of BHCD to CHDM

In the second step, BHCD with a certain purity (90%) obtained from the first step was converted to CHDM by the selective hydrogenation of ester group. However, it is well known that the hydroxyl group can be hydrogenated by the Cu-based catalysts,^{32,33} which make the second step difficult because of the



Fig. 4 Influence of stirring rate on the conversion of BHET and the yield of BHCD. Reaction conditions: 2.0 g BHET, 0.1 g Pd/C, 5.5 MPa, 428 K, and 2 h.

Paper

100

80

60

40

20

0

Conversion and yield (%)



Scheme 4 The possible reaction pathway for the hydrogenation of BHCD to CHDM.

hydroxyl groups in BHET. As shown in Scheme 4, we suggest the possible reaction pathway for the hydrogenation of BHCD to CHDM. The hydrogenation reaction follows two pathways: (i) the ester group in one side chain is firstly reduced to hydroxyl group, and then the other ester group is reduced, (ii) the terminal hydroxyl groups are firstly reduced and then the ester groups are reduced. The reaction pathway (i) and (ii) produce ethylene glycol and ethanol, respectively. The amount of ethylene glycol is much higher than ethanol, which implies that the reaction mainly follows pathway (i). We used Cu–Cr and Cu–Zn/Al₂O₃ as catalysts in the second step. In order to get the maximum yield of CHDM, we investigated the influences of different reaction conditions on the hydrogenation reaction of BHCD to CHDM.

3.2.1. Influence of reaction temperature. Fig. 5 shows the influence of reaction temperature on the conversion of BHCD and yield of CHDM catalyzed by Cu-Cr and Cu-Zn/Al2O3 catalysts. The conversion of BHCD reached almost 100% at the temperature of 543 K and 523 K catalyzed by Cu-Cr and Cu-Zn/ Al₂O₃ catalysts, respectively. However, the yield of CHDM initially increased and then decreased with the increase of the reaction temperature, due to the excessive hydrogenation of BHCD. A reaction temperature of 563 K is the best for the hydrogenation reaction, affording about 32% and 66% CHDM yield catalyzed by Cu-Cr and Cu-Zn/Al2O3 catalysts, respectively. When the temperature was higher than 563 K, the hydroxyl groups in CHDM would be further reduced, resulting in the increase of the by-products. Moreover, it is apparent that the yield of CHDM catalyzed by Cu-Zn/Al₂O₃ is much higher than that catalyzed by Cu-Cr catalyst.

3.2.2. Influence of reaction time. The influence of reaction time on the conversion of BHCD and yield of CHDM catalyzed



Fig. 5 Influence of reaction temperature on the conversion of BHCD and yield of CHDM. Reaction conditions: Cu–Cr: 2.0 g intermediate products (90% BHCD), 0.1 g Cu–Cr, 10 h, and 10 MPa; Cu–Zn/Al₂O₃: 2.0 g intermediate products (90% BHCD), 0.1 g Cu–Zn/Al₂O₃, 10 h, and 6.5 MPa.

by Cu–Cr and Cu–Zn/Al₂O₃ catalysts is shown in Fig. 6. It displays that the reaction time is a dominant parameter affecting the ultimate catalyst performance. The conversion of BHCD increased when the reaction time increased, whereas the yield of CHDM initially increased when the reaction time increased to 10 h and then decreased when the reaction time increased prolonged from 10 h to 12 h, which is attributed to the further hydrogenation of the hydroxyl group of CHDM. As a consequence, the preferred reaction time is 10 h, affording about 32% and 65% CHDM yield catalyzed by Cu–Cr and Cu– Zn/Al₂O₃ catalysts, respectively. It displays that the excessive increase of reaction time has no effect on the improvement of the yield of CHDM.

3.2.3. Influence of reaction pressure. Fig. 7 shows the influence of reaction pressure on the conversion of BHCD and yield of CHDM catalyzed by Cu–Cr and Cu–Zn/Al₂O₃ catalysts. The conversion of BHCD reached almost 100% when the



Fig. 6 Influence of reaction time on the conversion of BHCD and yield of CHDM. Reaction conditions: Cu–Cr: 2.0 g intermediate products (90% BHCD), 0.1 g Cu–Cr, 543 K, and 10 MPa; Cu–Zn/Al₂O₃: 2.0 g intermediate products (90% BHCD), 0.1 g Cu–Zn/Al₂O₃, 563 K, and 6.5 MPa.



Fig. 7 Influence of reaction pressure on the conversion of BHCD and yield of CHDM. Reaction conditions: Cu–Cr: 2.0 g intermediate products (90% BHCD), 0.1 g Cu–Cr, 543 K, and 10 h; Cu–Zn/Al₂O₃: 2.0 g intermediate products (90% BHCD), 0.1 g Cu–Zn/Al₂O₃, 563 K, and 6 h.

reaction pressure reached 2.5 MPa. It could be found that with the increase of the reaction pressure from 2.5 to 10.5 MPa, the yield of CHDM increased and then became unchanged without affecting the conversion of BHCD. It reveals that the high pressure greatly improves the selective hydrogenation of the ester groups in BHCD and decreases the by-products which resulted in the high yield of CHDM. Under the optimal reaction pressure of 10.5 MPa, the yield of CHDM reached 26% and 78% catalyzed by Cu–Cr and Cu–Zn/Al₂O₃ catalysts respectively.

3.2.4. Influence of stirring rate. Fig. 8 shows the influence of stirring rate on the conversion of BHCD and the yield of CHDM. As can be seen, the yield of BHCD firstly increased with the increase of the stirring rate from 50 to 300 rpm, and then kept about 52% from 300 to 600 rpm. However, the conversion of BHCD reached about 98% when the stirring rate was 50 rpm. The hydrogenation of BHCD to CHDM is a multi-step reaction, the previous reaction steps were performed with low stirring rate, however, the high stirring rate promoted the followed reaction steps, resulting in the increase of the yield of CHDM with the increase of the stirring rate. There should be no mass

Yield of CHDM Conversion of BHCD

500

600

400

300

Fig. 8 Influence of stirring rate on the conversion of BHCD and the

Stirring rate (rpm)

or heat transfer limitation with a stirring rate higher than 300 rpm in the hydrogenation.

Temperature

Fig. 9 TPR profiles of the Cu-Cr and Cu-Zn/Al₂O₃ catalysts before

 (\mathbf{K})

470

495

Hydrogen uptake (a.u.)

reduction

350 400 450 500 550 600 650 700 750

3.2.5. Characterization of Cu-based catalysts. The reducibility of the Cu–Cr and Cu–Zn/Al₂O₃ catalysts is shown in Fig. 9. The reduction peaks of the Cu–Cr and Cu–Zn/Al₂O₃ catalysts are 495 K and 470 K, respectively. It reveals that the Cu²⁺ species can be reduced *in situ* to Cu⁺ or/and Cu⁰ because the reduction temperature of Cu–Cr and Cu–Zn/Al₂O₃ catalysts in the experiment are of 623 K and 573 K which are higher than the reduction peaks of Cu–Cr and Cu–Zn/Al₂O₃ catalysts, respectively.

The XRD patterns of the Cu–Cr and Cu–Zn/Al₂O₃ catalysts before and after reduction are shown in Fig. 10 and 11, respectively. The typical diffraction peaks with 2θ indexed with approximately at 32.3, 36.2, 42.2, 53.6 and 58.1° in the Cu–Cr and Cu–Zn/Al₂O₃ catalysts before reduction which can be assigned to the crystalline phase of CuO. The appearance of Cu⁰ crystallite diffraction peaks at 43.29, 50.42 and 74.03° in the XRD patterns of the Cu–Cr and Cu–Zn/Al₂O₃ catalysts after reduction, clearly demonstrates that the Cu²⁺ is reduced to Cu⁰. While, the Cu⁺ diffraction peaks are also found. Therefore, the Cu⁺/Cu⁰ species are the active sites in our present catalytic system. Additionally, diffraction peaks belonging to Cr₂O₃ are



200

100



Fig. 10 XRD patterns of the Cu–Cr catalyst (a) before reduction (b) after reduction.

Cu/ZnO/Al2O

Cu-Cr

100

80

60

40

20

0

Conversion and yield (%)



Fig. 11 XRD patterns of the $Cu-Zn/Al_2O_3$ catalyst (a) before reduction (b) after reduction.

detectable in Fig. 10, it is suggested that Cr_2O_3 serve as supports in Cu–Cr catalyst. Moreover, there are no diffractions related to Al_2O_3 in Fig. 11 are observed, indicative of the presence of amorphous Al_2O_3 , the ZnO and amorphous Al_2O_3 phases may function as supports or dispering agents in the Cu–Zn/Al₂O₃ catalyst.

The Cu-based catalysts were characterized with low temperature N₂ adsorption–desorption to elucidate the structural features. As shown in Table 1, it displays that the surface area of the Cu–Zn/Al₂O₃ catalyst is larger than the Cu–Cr catalyst, which may be contributing to the higher activity of the Cu–Zn/Al₂O₃ catalyst than the Cu–Cr catalyst.

The optimal reaction conditions of the hydrogenation of BHCD to CHDM are 543 K, 10 h, and 10.5 MPa. The yield of CHDM and the conversion of BHCD have reached 32%, 78%, and 100% catalyzed by Cu-Cr and Cu-Zn/Al2O3 catalysts, respectively. Cu-Zn/Al₂O₃ catalyst shows much higher activity and selectivity of the hydrogenation of ester to alcohol than Cu-Cr catalyst, it is deduced that the addition of Zn and Al can improve the activity and selectivity of the Cu-based catalysts in the hydrogenation of ester group resulting in the increase of the yield of CHDM. On the contrary, the addition of Cr can improve the activity and selectivity of the Cu-based catalyst in the hydrogenation of hydroxyl group resulting in the decrease of the yield of CHDM. In addition, Cu-Zn/Al2O3 catalyst is more environmentally friendly than Cu-Cr catalyst. Therefore, we choose Cu-Zn/Al₂O₃ as the excellent catalyst in the hydrogenation reaction of BHCD to CHDM.

 Table 1
 BET surface area, pore volume and mean pore size of the Cubased catalysts

Sample	Surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Mean pore size (nm)
Cu–Cr	10.88	0.09	33.8
Cu–Zn/Al ₂ O ₃	33.52	0.15	16.4

4. Conclusions

On the basis of the above discussion, it is shown that the waste PET monomer BHET can be efficiently converted into CHDM by a two-step hydrogenation reaction using Pd/C and Cu-based catalysts without solvent. The conversion of BHET and the yield of CHDM have reached as high as 100% and 78%, respectively. The phenyl group can be efficiently hydrogenated to cyclohexane group catalyzed by Pd/C catalyst under relative mild conditions in the first step. However, the competition of hydroxyl and ester groups in the reaction with hydrogen increases the difficulty of the selective hydrogenation of ester groups in the second step. The Cu-Zn/Al₂O₃ catalyst shows much higher activity and selectivity of the hydrogenation of ester group to hydroxyl group than Cu-Cr catalyst. Moreover, it is suggested that the Cu⁺/Cu⁰ species are the active sites in the Cu-based catalysts. In summary, it is successfully converted the waste PET monomer BHET to high-valued CHDM, thus providing not only a new method for the production of CHDM, but also another direction for the chemical recycling of waste PET.

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Notes and references

- 1 S. R. Turner, J. Polym. Sci., Part A: Polym. Chem., 2004, 42, 5847–5852.
- 2 H. J. Bang, H. Y. Kim, F. L. Jin and S. J. Park, *J. Ind. Eng. Chem.*, 2011, **17**, 805–810.
- 3 L. H. Zhu, L. Zheng, K. Q. Du, H. Fu, Y. H. Li, G. R. You and B. H. Chen, *RSC Adv.*, 2013, **3**, 713–719.
- 4 Y. J. Zhao, J. Zhou, J. G. Zhang, D. Y. Li and S. D. Wang, *Ind. Eng. Chem. Res.*, 2008, 47, 4641–4647.
- 5 S. K. Sharma, K. B. Sidhpuria and R. V. Jasra, *J. Mol. Catal. A: Chem.*, 2011, **335**, 65–70.
- 6 M. Saeys, M. F. Reyniers, M. Neurock and G. B. Marin, *J. Phys. Chem. B*, 2005, **109**, 2064–2073.
- 7 Y. Q. Huang, Y. Ma, Y. W. Cheng, L. J. Wang and X. Li, *Ind. Eng. Chem. Res.*, 2014, **53**, 4604–4613.
- 8 P. Kasinathan, D. W. Hwang, U. H. Lee, Y. K. Hwang and J.-S. Chang, *Catal. Commun.*, 2013, **41**, 17–20.
- 9 J. L. Gong, H. R. Yue, Y. J. Zhao, S. Zhao, L. Zhao, J. Lu, S. P. Wang and X. B. Ma, *J. Am. Chem. Soc.*, 2012, 134, 13922–13925.
- 10 P. Yuan, Z. Y. Liu, W. Q. Zhang, H. J. Sun and S. C. Liu, *Chin. J. Catal.*, 2010, **31**, 769–775.
- M. Toba, S.-i. Tanaka, S.-i. Niwa, F. Mizukami, Z. Koppány,
 L. Guczi, K.-Y. Cheah and T.-S. Tang, *Appl. Catal.*, A, 1999,
 189, 243–250.

- 12 K. Tahara, H. Tsuji, H. Kimura, T. Okazaki, Y. Itoi, S. Nishiyama, S. Tsuruya and M. Masai, *Catal. Today*, 1996, **28**, 267–272.
- 13 M. J. Hanton, S. Tin, B. Boardman and P. Miller, *J. Mol. Catal. A: Chem.*, 2011, 346, 70–78.
- 14 S. Chakraborty, H. Dai, P. Bhattacharya, N. T. Fairweather, M. S. Gibson, J. A. Krause and H. Guan, *J. Am. Chem. Soc.*, 2014, **136**, 7869–7872.
- 15 Z. Q. Zhu, Z. H. Lu, B. Li and S. Z. Guo, *Appl. Catal.*, A, 2006, 302, 208–214.
- 16 R. Raja, T. Khimyak, J. M. Thomas, S. Hermans and B. F. G. Johnson, *Angew. Chem., Int. Ed.*, 2001, **40**, 4638–4642.
- 17 A. B. Hungria, R. Raja, R. D. Adams, B. Captain, J. M. Thomas, P. A. Midgley, V. Golovko and B. F. G. Johnson, *Angew. Chem., Int. Ed.*, 2006, 45, 4782–4785.
- 18 X. F. Li, Z. Y. Sun, J. L. Chen, Y. Zhu and F. Z. Zhang, *Ind. Eng. Chem. Res.*, 2014, 53, 619–625.
- 19 M. L. Zhu, Z. X. Li, Q. Wang, X. Y. Zhou and X. M. Lu, *Ind. Eng. Chem. Res.*, 2012, **51**, 11659–11666.
- 20 M. L. Zhu, S. Li, Z. X. Li, X. M. Lu and S. J. Zhang, *Chem. Eng. J.*, 2012, **185**, 168–177.
- 21 G. X. Xi, M. X. Lu and C. Sun, *Polym. Degrad. Stab.*, 2005, **87**, 117–120.

- 22 M. Ghaemy and K. Mossaddegh, *Polym. Degrad. Stab.*, 2005, **90**, 570–576.
- 23 Q. Wang, X. Q. Yao, S. F. Tang, X. M. Lu, X. P. Zhang and S. J. Zhang, *Green Chem.*, 2012, **14**, 2559–2566.
- 24 H. Wang, Y. Q. Liu, Z. X. Li, X. P. Zhang, S. J. Zhang and Y. Q. Zhang, *Eur. Polym. J.*, 2009, **45**, 1535–1544.
- 25 H. Wang, Z. X. Li, Y. Q. Liu, X. P. Zhang and S. J. Zhang, *Green Chem.*, 2009, **11**, 1568–1575.
- 26 S. R. Shukla, A. M. Harad and L. S. Jawale, *Waste Manag.*, 2008, **28**, 51–56.
- 27 N. M. Abdullah and I. Ahmad, *Fibers Polym.*, 2013, **14**, 584–590.
- 28 S. R. Shukla, A. M. Harad and L. S. Jawale, *Polym. Degrad. Stab.*, 2009, **94**, 604–609.
- 29 Y. Kai and A. C. Chen, *Energy*, 2013, 58, 357-363.
- 30 L. M. He, H. Y. Cheng, G. F. Liang, Y. C. Yu and F. Y. Zhao, *Appl. Catal.*, A, 2013, 452, 88–93.
- 31 H. Z. Liu, T. Jiang, B. X. Han, S. G. Liang and Y. X. Zhou, *Science*, 2009, **326**, 1250–1252.
- 32 Z. H. Xiao, X. K. Wang, J. H. Xiu, Y. M. Wang, C. T. Williams and C. H. Liang, *Catal. Today*, 2014, **234**, 200–207.
- 33 R. V. Sharma, P. Kumar and A. K. Dalai, *Appl. Catal.*, A, 2014, 477, 147–156.