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Selective synthesis of 1,3-propanediol from glycidol over a carbon film encapsulated Co catalyst[†]

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1,3-Propanediol (1,3-PDO) is an important chemical and feedstock in the synthesis of polytrimethylene terephthalate (PTT) resin, but the catalytic production of 1,3-PDO is difficult. In this work, a carbon film encapsulated Co nanoparticle catalyst (Co@NC) was synthesized *via* pyrolysis of Co₂(1,4-benzenedicarboxylic acid)₂(triethylenediamine) and tested in the synthesis of 1,3-PDO from glycidol. It was found that this Co@NC catalyst was highly active, selective and stable for this reaction under mild conditions. Characterization results indicated that the formation of 1,3-PDO was sensitive to the adsorbed hydrogen. The selectivity to 1,3-PDO reached its maximum over the Co@NC catalyst as carbon film encapsulation can inhibit the excessive adsorption and activation of H₂ molecules, while the adsorbed dissociated hydrogen on naked Co NPs and/or N atoms (in the carbon shell) promoted the formation of propanol.

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1 Introduction

1,3-Propanediol (1,3-PDO) is an important chemical for its application in pharmaceuticals, plasticizers, surfactants, emulsifiers and demulsifiers. More importantly, 1,3-PDO is an indispensable monomer for production of polytrimethylene terephthalate (PTT) resin, a new type of polyester which exhibits good light stability, softness, bulkiness, pollution resistance, and dyeability,^{1,2} and much better resilience and stress/recovery properties than polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).³ These excellent properties of PTT make it more competitive in the production of new textiles, carpets, fibers, films, and thermoplastics.⁴ As one of the feedstocks of PTT, the potential market capacity of 1,3-PDO was estimated to be more than 2.27 million tons in 2020 and the synthesis of 1,3-PDO has attracted great attention in recent years.

1,3-PDO can be chemically synthesized *via* the hydroformylation of ethylene oxide followed by hydrogenation, or *via* the hydration of acrolein to 3-hydroxypropionaldehyde followed by aldehyde hydrogenation.⁵ But the main drawback of these petroleum-based routines lies in the low selectivity. Currently, bacterial fermentation of glycerol is a relatively well-developed approach to obtain 1,3-PDO in high yield. Nevertheless, the biological fermentation has a low metabolic efficiency because the reaction proceeds slowly in two steps.^{4,6} In addition, the catalytic selective hydrogenolysis of glycerol to 1,3-PDO over a heterogeneous catalyst has become a hot topic in the past decade.

Glycerol, an excessively generated by-product during the production of soap and biodiesel,^{7,8} is one of the top twelve biomass-derived building blocks.9 In published studies, many efforts were reported on the catalytic hydrogenolysis of the C-O bond in glycerol, and the obtained products included 1,2-propanediol (1,2-PDO), 1,3-PDO, 1-propanol (1-PO), 2-propanol (2-PO), ethanol and propane.¹⁰⁻¹³ However, a large number of catalytic systems gave high yields of 1,2-PDO and propanol as the major products,¹⁴⁻¹⁶ and considerable studies have been carried out in order to increase the yield of 1,3-PDO via the direct hydrogenolysis of glycerol. At the moment, the most effective strategy is bifunctional catalytic systems consisting of an active noble metal (Ir, Rh, or Pt) and oxophilic additives (mainly MoO_x , ReO_x or WO_x).^{2,17-22} Among which, it was found that the selectivity toward 1,3-PDO was 51.6% (with an 81.4% conversion of glycerol) over 0.10AuPt/WO_x under relatively mild conditions (140 °C, 1 MPa H_2).²³ On the surface of a WO_x-supported single/ pseudo-single atom Pt catalyst, the space-time yield toward 1,3-PDO reached 3.78 g g_{Pt}^{-1} h⁻¹.²⁴ The yield of 1,3-PDO over Ir-ReO_x/SiO₂ reached 38% with 81% conversion of glycerol at 8 MPa H₂ and 120 °C.² At a higher temperature (200 °C), it was reported that the yield of 1,3-PDO could reach 38.5% over Pt/WO_x/Al₂O₃ (at 9 MPa H₂ and 4 h).²⁵ Until now, the highest yield of 1,3-PDO in the literature reached 66% (with a complete conversion of glycerol, over Pt/WO_x/AlOOH at 5

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MPa H₂, 180 °C and Pt/glycerol = 0.9%).²⁶ Therefore, the direct hydrogenolysis of glycerol to 1,3-PDO is still a challenging task, and there is a strong motivation to explore new alternative methods to obtain 1,3-PDO in high yield.

It has been reported that cyclic ethers with an adjacent -CH₂OH group, such as tetrahydrofurfuryl alcohol and 2-(hydroxymethyl)tetrahydropyran, can be selectively hydrogenated to their corresponding α - ω diols, *i.e.* 1,5-pentanediol and 1,6-hexanediol over Rh-ReO_x/C, Rh-ReO_x/SiO₂ or Ir-ReO_x/SiO₂ catalysts.^{17,27-29} And it was proposed that this route was performed in a consecutive ring opening at the C-O bond neighboring -CH₂OH group, followed by hydrogenation to form the α - ω diols.

Glycidol, a derivative of glycerol, can be easily prepared from glycerol over mixed oxides of Ba, Ce, and/or ionic liquid catalysts, and the reported yield of glycidol was higher than 80%.³⁰⁻³⁴ Moreover, glycidol can also be synthesized easily from 2-chloro-1,3-propanediol (β-MCH, a by-product during the production of epichlorohydrin from glycerol), and the selectivity of glycidol reached 99% within 30 minutes even at room temperature.35 Glycidol could be selectively converted to 1,2-PDO via a hydrogenolysis reaction over noble metal-based Pd/C or Pd/C + Amberlyst-15 catalysts.^{36,37} In 2017, Gebretsadik found that 1,3-PDO could be synthesized via the hydrogenation of glycidol, and the highest yield of 1,3-PDO over a saponite supported Ni catalyst reached 29% at 180 °C.38 More recently, it was found that the yield of 1,3-PDO could be further increased to 46.1% over a ReO_x modified Ni catalyst.³⁹ These pioneering studies paved a new strategy for the synthesis of 1,3-PDO from renewable feedstocks.

Recently, carbon-based materials become a research hotspot due to their unique properties, such as large specific surface area, superior electrical conductivity, extraordinary mechanical flexibility, chemical stability and easy functionalization. These carbon materials have been widely used in many fields such as catalysis,^{40,41} lithium-sulfur batteries,42 lithium ion batteries,43 electromagnetic wave shielding,44 multifunctional polymer composites,45,46 microwave-adsorbing ceramic composites,⁴⁷ metacomposites,48,49 and sizing agents.50 Among which, graphene encapsulated metal catalysts exhibit high stability under harsh conditions due to their unique core-shell structure, and the synthesis and application of this type of catalyst has attracted extensive attention.

In this work, a carbon film encapsulated Co nanoparticle (NP) catalyst (Co@NC) was synthesized *via* the pyrolysis of Co₂(bdc)₂(ted) (bdc: 1,4-benzenedicarboxylic acid; ted: triethylenediamine) (see Fig. 1), and it was tested in the synthesis of 1,3-PDO from glycidol. It was found that the Co@NC catalyst was highly active, selective and stable for the formation of 1,3-PDO among the tested Pt-, Pd-, Co-, Ni-, Cu- and Rubased catalysts under mild conditions. The reaction mechanism and structure–performance relationship of this Co@NC catalyst were discussed on the basis of a series of characterization and controlled experiments.



Fig. 1 Schematic illustration of the synthesis of Co@NC.

2 Experimental

2.1 Catalyst preparation

Synthesis of Co@NC. Typically, 6.0 g of Co(NO₃)₂·6H₂O, 3.5 g of 1,4-benzenedicarboxylic acid and 1.12 g of triethylenediamine were dispersed in 100 mL N.Ndimethylmethanamide (DMF) by stirring. Subsequently, the solution was sealed in a Teflon-lined autoclave and subjected to a solvothermal reaction at 120 °C in an oil bath and kept stirring for 2 days. After that, the autoclave was cooled to room temperature and the resultant precipitates were collected by filtration. The solid precipitates were immersed in 100 mL anhydrous methanol to undergo solvent exchange at 70 °C for 3 h. Finally, the solid sample was dried in a vacuum at 60 °C for 20 h, and denoted as Co₂(bdc)₂(ted).

A carbon film encapsulated Co NP catalyst (identified as Co@NC) was prepared by pyrolyzing the $Co_2(bdc)_2(ted)$ precursor in a N₂ atmosphere at 700 °C for 2 h with a heating rate of 2 °C min⁻¹.

Synthesis of Co@NG-ZIF. Co@NG-ZIF, as a reference catalyst with a higher N content in its framework, was prepared in a similar procedure to that of Co@NC. Typically, 4.47 g of $Co(NO_3)_2$ · $6H_2O$ and 9.84 g of 2-methylimidazole were dissolved in 100 mL anhydrous methanol. The solution was subjected to stirring for 10 h at room temperature and then kept static for 12 h. The purple solid precursor was obtained by centrifugation and dried in a vacuum at 60 °C for 20 h. Co@NG-ZIF was prepared *via* pyrolyzing this precursor at 700 °C for 2 h with a heating rate of 2 °C min⁻¹.

Synthesis of other reference catalysts. Other cobalt-based catalysts supported on active carbon (AC), Al_2O_3 , MgO, ZnO, MCM-41, H-BEA and multiwall carbon nanotubes (MWCNTs) were prepared *via* a wetness impregnation method using $Co(NO_3)_2$ · $6H_2O$ as a precursor. Typically, these supports were impregnated with appropriate amounts of precursor solution (mass ratio of Co/support was controlled at 15%). At the same time, a series of reference catalysts, such as MWCNT supported Ni, Cu, Pt, Pd, and Ru catalysts, were prepared *via* a wetness impregnation method using Ni(NO₃)₂, Cu(NO₃) ₂, H₂PtCl₆, PdCl₂, and RuCl₃ as precursors (mass ratio of Ni and Cu/support = 15%, and Pt, Pd and Ru/support = 4%). Before the catalytic reaction, the impregnated samples were dried at

80 °C overnight, calcined in N_2 or air (for carbon supports and other inorganic supports, respectively), and then reduced in H_2 .

2.2 Characterization

Power X-ray diffraction (XRD) patterns of the parent Co₂(bdc)₂(ted) and other Co-based catalysts were detected at room temperature on a Rigaku D/WAX-2500 diffractometer using Cu K α radiation (λ = 1.5406 Å) with a 2 θ step of 0.02°. N₂ adsorption was measured at its normal boiling point using an ASAP 2010 analyzer (Micromeritics). Before the N2 adsorption test, the parent Co₂(bdc)₂(ted) and the Co@NC catalyst were pretreated at 100 °C and 150 °C for 4 h under vacuum, respectively. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore volume and pore size distribution were calculated by the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analysis (TGA) of Co₂(bdc)₂(ted) was carried out on a Netzsch STA 409 thermobalance from room temperature to 800 °C at a heating rete of 5 °C min⁻¹ in a N₂ flow. Scanning electron microscopy (SEM) images were detected on a Leo Evo Series SEM (VP 1430, Germany). Transmission electron microscopy (TEM, JEOL-2010F) was employed to observe the morphologies and dimensions of the catalysts by using an accelerating voltage of 200 kV.

X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI ESCA system. The X-ray source was a Mg standard anode 146 (1253.6 eV) at 12 kV and 300 W. The actual content of Co and other metals in the prepared catalysts was detected on inductively coupled plasma atomic emission spectroscopy equipment (ICP, plasma-Spec-II spectrometer, Perkin-Elmer Optima 2000 instrument) according to the following procedure. 0.1 g of sample was pretreated in air from room temperature to 900 °C, then the residual solids were dissolved with 50 mL *aqua regia* solution. Metal ions in the above solution were detected *via* ICP, and these data are summarized in Table S1.†

H₂ activation activity of the prepared Co@NC, Co/AC, and Co@NG-ZIF catalysts was characterized *via* temperatureprogrammed desorption of H₂ (H₂-TPD), which was performed in a home-made microreactor equipped with a mass spectrometer (OmniStar GSD301, Switzerland). 0.1 g of sample was first pretreated at 450 °C for 1 h in an Ar atmosphere and then cooled to 30 °C. After that, the sample was exposed to H₂ for 1 h. Then, the reactor was purged by Ar at 30 °C for 1.5 h to eliminate the physically adsorbed H₂. H₂-TPD was conducted by ramping to 350 °C at 10 °C min⁻¹. The concentration of H₂ (*m*/*z* = 2) in the effluent was recorded using a mass spectrometer.

2.3 Catalytic reaction

The selective hydrogenation of glycidol over different catalysts was carried out in a 100 mL Teflon-lined stainless autoclave. In a typical procedure, 0.3 g of glycidol and a certain amount of the catalyst were dispersed in 10 mL ethanol, and the mass ratio of Co, Ni, and Cu/glycidol = 9.8 wt%, Pt, Pd, and Ru/glycidol = 0.66 wt%. After the reactor was sealed, air was purged by flushing three times with 2.0 MPa H₂, then the autoclave was pressurized with 2.0 MPa H₂, and stirred at 120 °C. After the reaction, the reactor was cooled to room temperature and depressurized carefully. The gas phase was collected and analyzed using a gas chromatograph (Shimadzu, 8A) equipped with a TCD detector. n-Butanol was added as an internal standard to the reaction liquid. The mixture was quantitatively analyzed with a gas chromatograph (Shimadzu, 14B) which was equipped with a 30 m capillary column (DB-WAX 52 CB, USA) and flame ionization detector. At the same time, GC-MS analysis confirmed that the reaction mixture contained glycidol, 1-PO, 1,2-PDO, 1,3-PDO and ring-opening products via the alcoholysis reaction between glycidol and solvent (ethanol), i.e., 3-ethoxy-1,2propanediol (RO1) and 2-ethoxy-1,3-propanediol (RO2). No condensation by-product of glycidol was detected in the reaction mixture. In view of the irreversible formation of RO1 and RO2 even in a blank experiment (without a catalyst), RO1 and RO2 were regarded as the unreacted glycidol when calculating the conversion of glycidol and the selectivity to products. In this case, the conversion of glycidol was calculated on the basis of the formed 1-PO, 1,2-PDO and 1,3-PDO, as follows:

Conversion = (total moles of formed 1-PO, 1,2-PDO, and 1,3-PDO)/(moles of glycidol added) × 100%.

Selectivity = (moles of one product)/(moles of glycidol converted) × 100%.

The specific activity of the added catalyst, turnover frequency (TOF), was calculated as follows:

TOF = (moles of glycidol converted)/(moles of total metal atoms)/(reaction time).

For each successive use, the catalyst was washed with ethanol three times, followed by drying in a vacuum at 60 °C overnight. The procedure of the controlled experiments, such as hydrogenation of 1,2-PDO, 1,3-PDO and propylene oxide, was similar to that above, but using 1,2-PDO, 1,3-PDO and propylene oxide as the starting substrates.

3 Results

3.1 The structure of the Co₂(bdc)₂(ted) precursor

At first, $Co_2(bdc)_2$ ted was fabricated by traditional solvothermal methods according to ref. 51. XRD analysis found that the diffraction peaks of the synthesized $Co_2(bdc)_2(ted)$ matched well with the simulated pattern given in the literature, confirming its well crystallized structure (Fig. 2).^{52,53} The coordination environment of $Co_2(bdc)_2(ted)$ is shown in Fig. S1,† that is, four oxygen atoms from bdc and



Fig. 2 XRD patterns of simulated and as-synthesized $Co_2(bdc)_2(ted)$.

one nitrogen atom from ted are coordinated with each Co atom. Moreover, it was noteworthy that all peaks (except for (001)) shifted to lower 2θ values, which should be attributed to the unusual guest-dependent dynamic behavior of $Co_2(bdc)_2$ ted: the framework expands upon guest (DMF) release and shrinks upon guest inclusion.⁵² In this work, the synthesized $Co_2(bdc)_2(ted)$ was subjected to solvent exchange with methanol and drying in a vacuum, which resulted in the expansion of the framework and the smaller diffraction angles as DMF molecules were removed.

The quadrangular prism-shaped structure of Co₂(bdc)₂-(ted) was confirmed in its typical SEM image (Fig. S2[†]). The N₂ adsorption-desorption isotherm of Co₂(bdc)₂(ted) was a type I model with a rapid increase of N₂ adsorption quantity at the P/P_0 range of 0–0.01 (Fig. S3⁺), which corresponded to its microporous structure. In addition, the calculated BET surface area of Co₂(bdc)₂(ted) was 1700 m² g^{-1} . Thermogravimetric analyses (TGA) indicated that there were two major mass losses during the themolysis of $Co_2(bdc)_2(ted)$ (Fig. S4[†]). The first mass loss (23.6%) at 25-400 °C was attributed to the volatilization of water,^{54,55} and the other abrupt mass loss (about 44.7%) was observed between 400 and 505 °C, indicating that the entire structure of Co₂(bdc)₂(ted) underwent drastic thermal decomposition. And the mass of the remaining catalyst changed slightly after 700 °C.

3.2 The fine structure of the Co@NC catalyst

Fig. 3 shows the XRD pattern of the Co@NC catalyst. It was found that mainly metallic Co was detected in Co@NC, and the characteristic diffraction peaks at 44.5, 51.8 and 76.4° corresponded to the (111), (200) and (220) crystalline plane reflections of $\text{Co}^{0,56,57}$ respectively. These results demonstrated that Co^{2+} could be reduced to the metallic phase *via* carbothermic reduction under the pyrolysis conditions. The average crystalline size of Co in Co@NC was calculated to be 23.1 nm according to the Scherrer equation. The content as well as the particle size of Co in Co@NC and other reference catalysts is summarized in Table S1.†



Nitrogen adsorption-desorption analysis (Fig. 4) showed that Co@NC had a typical type IV isotherm with a H₄-type hysteresis loop at the P/P_0 range of 0.5–1.0. These results confirmed that Co@NC was a mesoporous material. The specific surface area of Co@NC was 130 m² g⁻¹, and its cumulative mesopore volume reached 0.1802 cm³ g⁻¹. The calculated mesopore size in Co@NC was 3.9 nm (Fig. 4, inset).

The morphology of the Co@NC catalyst was observed by SEM (Fig. 5a). It can be found that Co@NC maintained the quadrangular prism-shaped structure similar to the parent $Co_2(bdc)_2(ted)$ (Fig. S2†). TEM analysis disclosed that the Co@NC catalyst was composed of spherical Co NPs embedded in the thick carbon matrix (Fig. 5b and c), in which Co NPs have sizes of 13–35 nm. HRTEM images further disclosed that those Co NPs were encapsulated in a layer of carbon film (around 1.0–1.2 nm) (Fig. 5d). The average size of Co NPs in Co@NC was estimated to be 25.6 nm from the TEM analysis of over 300 randomly selected particles.

3.3 Hydrogenation of glycidol over different catalysts

Table 1 summarizes the performance of Co@NC and MWCNT supported Pt-, Pd-, Co-, Ni-, Cu-, Ru-based catalysts



Fig. 4 $\,N_2$ adsorption-desorption isotherm and pore size distribution (inset) of the Co@NC catalyst.



Fig. 5 (a) SEM and (b–d) TEM images of Co@NC (the scale bar in Fig. d is 10 nm).

for the hydrogenation of glycidol at 2.0 MPa H₂ and 120 °C. It can be found that Pt- and Pd-based catalysts were active for the hydrogenation of glycidol, and the highest conversion of glycidol (in 5 h) reached 69.6% over Pt/MWCNTs, but mainly 1,2-PDO formed in the reaction mixture. On the other hand, Ni-, Cu- and Ru-based catalysts were less active under the same reaction conditions. It is quite interesting to note that Co/MWCNTs were selective for the formation of 1,3-PDO from glycidol, and the selectivity to 1,3-PDO was 50.4% (with a 43.4% conversion of glycidol). Furthermore, the carbon film encapsulated Co catalyst (Co@NC) was more active and selective for this reaction, and the selectivity to 1,3-PDO increased to 59.0% (with a 61.0% conversion of glycidol). These results indicated that the Co-based catalyst was promising for the selective hydrogenation of glycidol to 1,3-PDO. A blank experiment without a catalyst was carried out under the same conditions (Table 1, entry 1). No hydrogenation products (1,3-PDO, 1,2-PDO and 1-PO) were detected except the alcoholysis products (RO1 and RO2), which indicated that those carbon film encapsulated Co NPs were the indispensable active sites in the hydrogenation of glycidol. The alcoholysis reaction of glycidol could occur without a catalyst at 120 °C, and it seems that the formation of RO1 and RO2 is spontaneous.

3.4 Hydrogenation of glycidol over Co-based catalysts

Table 2 compares the performance of Co-based catalysts that were supported on active carbon (AC), and traditional oxides or zeolites (ZnO, Al₂O₃, MgO, MCM-41, and H-BEA) for the selective hydrogenation of glycidol. Once again, it was confirmed that the Co-based catalyst was selective for the formation of 1,3-PDO from glycidol (except Co/AC and Co@NG-ZIF). And carbon material supported Co catalysts, such as Co@NC, Co/AC and Co/MWCNTs, were more active than oxide supported Co NPs. The carbon film encapsulated Co catalyst (Co@NC) still exhibited the best performance as it provided a high activity (61.0% conversion) and the highest selectivity toward 1,3-PDO (59.0%) (entry 1). On the other hand, the conversion of glycidol decreased to 53.5% over commercial AC supported Co catalysts (entry 2, Co/AC), and the selectivity toward 1,3-PDO was only 37.8%, the selectivity to less valuable and undesired 1-PO increased to 53.6%. What's more, the selectivity to 1,3-PDO decreased sharply to 11.0% over Co@NG-ZIF, while the selectivity to 1-PO was as high as 85.9% despite its highest activity (entry 3, 65.0% conversion at 2 h). Traditional oxide (ZnO, Al₂O₃, and MgO) or zeolite (MCM-41 and H-BEA)-supported Co-based catalysts can catalyze the hydrogenation of glycidol to 1,3-PDO with a selectivity of 40-56%, but the corresponding hydrogenation rates were quite low. As listed in entries 4-8, the conversion of glycidol over these supported Co catalysts was less than 28.4%. These results demonstrated that the nature of the support played a crucial role in the hydrogenation of glycidol.

In order to disclose the different product distributions during the hydrogenation of glycidol, the time courses over Co@NC, Co/AC and Co@NG-ZIF are compared in Fig. S5.† It was interesting to note that 1,3-PDO was the major product over Co@NC from the beginning of the reaction (Fig. S5(a)†). On the other hand, mainly 1-PO formed over Co/AC and Co@NG-ZIF (Fig. S5(b) and (c)†). These results indicated that 1-PO was the main by-product, and the challenge in the selective hydrogenation of glycidol to 1,3-PDO over Co-based catalysts lies in suppressing the formation of 1-PO.

Subsequently, the hydrogenation of glycidol under various H_2 pressures, temperatures, prolonged reaction times, and

Table 1 S	Selective hydrogenation of glycidol over different metal catalysts ^a								
Entry	Catalyst	Conv. (%)	$\mathrm{TOF}^{b}\left(\mathrm{h}^{-1} ight)$	Selectivity (%)					
				1,3-PDO	1,2-PDO	1-PO			
1		0	0						
2	Pt/MWCNTs	69.6	55.53	0.9	74.3	24.8			
3	Pd/MWCNTs	49.6	21.59	5.7	88.0	6.3			
4	Co/MWCNTs	43.4	0.7046	50.4	12.0	37.6			
5	Ni/MWCNTs	23.9	0.3864	28.1	67.9	4.0			
6	Cu/MWCNTs	14.5	0.2539	2.2	4.2	93.6			
7	Ru/MWCNTs	7.9	3.266	40.4	23.4	36.2			
8	Co@NC	61.0	0.9903	59.0	9.3	31.7			

^{*a*} Reaction conditions: 0.3 g glycidol in 10.0 mL ethanol with 9.8 wt% of Co, Ni, Cu, or 0.66 wt% of Pt, Pd, Ru, 2.0 MPa H₂, 120 °C, 5 h. ^{*b*} TOF was calculated on the basis of total metal atoms: TOF = (moles of glycidol converted)/(moles of total metal atoms)/(5 h).

 Table 2
 Selective hydrogenation of glycidol over different Co-based catalysts^a

Entry	Catalyst	Conv. (%)	$_{(\mathrm{h}^{-1})^c}^{\mathrm{TOF}}$	Selectivity (%)		
				1,3-PDO	1,2-PDO	1-PO
1	Co@NC	61.0	0.9903	59.0	9.3	31.7
2	Co/AC	53.5	0.8685	37.8	8.6	53.6
3	$Co@NG-ZIF^b$	65.0	2.6381	11.0	3.1	85.9
4	Co/ZnO	28.4	0.4611	55.2	17.8	27.0
5	Co/MCM-41	11.9	0.1932	47.3	6.1	46.6
6	Co/Al_2O_3	7.5	0.1218	54.6	7.1	38.3
7	Co/H-BEA	3.6	0.0584	56.1	5.3	38.6
8	Co/MgO	0.6	0.0097	41.4	43.4	15.2

^{*a*} Reaction conditions: 0.3 g glycidol in 10.0 mL ethanol with 9.8 wt% of Co, 2.0 MPa H₂, 120 °C, 5 h. ^{*b*} 2 h. ^{*c*} TOF was calculated on the basis of total Co: TOF = (moles of glycidol converted)/(moles of total Co atoms)/(reaction time).

different catalyst loadings was investigated in detail. Fig. S6† shows that the conversion of glycidol and the yield of 1,3-PDO increased obviously from 46.5% and 27.8% (at 1 MPa) to 67.3% and 41% (at 3 MPa), respectively while the yield of 1,2-PDO and 1-PO increased slightly from 4.9% and 13.8% (at 1 MPa) to 6.3% and 20% (at 3 MPa). Then the excellent performance of Co@NC was further confirmed under various reaction times at 100 °C, 120 °C and 140 °C (Fig. S7[†]). It can be found that 1,3-PDO was the dominant product over the Co@NC catalyst in all experiments and the yield of 1,3-PDO increased continuously with the reaction time. The detected conversion of glycidol was as high as 83.6% and the best yield of 1,3-PDO reached 50.4% at 140 °C, 4 h (Fig. S7(c)[†]). Regrettably, the calculated conversion of glycidol and the yield of 1,3-PDO cannot be increased with the prolonged reaction time (above 4 h) because of the competitive formation of 3-ethoxy-1,2-propanediol (RO1) and 2-ethoxy-1,3propanediol (RO2) between glycidol and solvent. These results meant that the reaction ended because there was no free glycidol in the reaction mixture. Fig. S8[†] shows that the conversion of glycidol increased rapidly from 24.4% to 83.6%, and the yield of all the products increased simultaneously as the loading of Co increased from 2.0 wt% to 9.8 wt%. However, these data changed slightly with excess catalysts, which might be attributed to the competitive alcoholysis reaction of glycidol.

Table S2† compares the previously published results with those obtained in this work. First, it was found that 1,2-PDO was the major product when the hydrogenation reaction was catalyzed by noble metal-based Pd/C or Pd/C-A15 catalysts, which matched well with our conclusion (Table 1, entry 3). The selectivity to 1,3-PDO reached 26% over the saponitesupported Ni catalyst (Ni(40)/Sap). More recently, it was found that the selectivity to 1,3-PDO increased to 47% over a ReO_xmodified Ni catalyst (NiRe(7)/MS). In this work, the selectivity to 1,3-PDO reached up to 60.3% over Co@NC, and the best yield of 1,3-PDO was 50.4%, which was better than the results in published studies.

The stability of the Co@NC catalyst was investigated to assess its potential in the hydrogenation of glycidol, and the performance of recycled Co@NC is shown in Fig. 6. No obvious loss of activity and selectivity toward 1,3-PDO was observed during the successive seven runs. The excellent stability of the Co@NC catalyst could be ascribed to the fact that Co NPs were well encapsulated in the carbon film, which protected the Co NPs from sintering, leaching or oxidation during the reaction process. The spent catalyst after 7 cycles was characterized, and the morphology of recycled Co@NC is shown in Fig. S9.† It was confirmed that the core–shell structure in Co@NC was well preserved. XRD analysis also indicated that metallic Co was still the dominant phase in this spent Co@NC (Fig. S10†).

4 Discussion

The above experiments indicated that Co-based catalysts were selective for the formation of 1,3-PDO from glycidol. Among which, the best yield of 1,3-PDO reached 50.4% over the carbon film encapsulated Co NP catalyst (Co@NC). At the same time, it was found that the fine structure of the Co based catalysts played a crucial role for the selective formation of 1,3-PDO. It is of great importance to disclose the real reason for the opposite product distribution over Co@NC (mainly 1,3-PDO formed) and Co@NG-ZIF (mainly 1-PO formed).



Fig. 6 Recycling of Co@NC for the selective hydrogenation of glycidol. Reaction conditions: 0.3 g glycidol in 10.0 mL ethanol with 9.8 wt% of Co, 2.0 MPa H_2 , 120 °C, 5 h.

Undoubtedly, PDOs were derived from the cleavage and hydrogenation of one C-O bond in the glycidol. However, the controversy was that 1-PO may be generated via the hydrogenolysis of PDOs and/or the simultaneous cleavage and hydrogenation of two C-O bonds in glycidol. In this case, a series of controlled experiments were carried out in order to disclose the formation pathway of 1-PO. At first, 0.3 g of 1,3-PDO or 0.3 g of 1,2-PDO was separately used as the starting material to be subjected to hydrogenation over Co@NC, Co/AC, and Co@NG-ZIF catalysts for 4 h under 2.0 MPa H₂ and 140 °C, and the results are summarized in Table S3.† It was found that no 1-PO was detected in the reaction mixture (Table S3,† entry 1-6). Therefore, it could be concluded that 1,3-PDO and 1,2-PDO were stable under the reaction conditions (140 °C), and all three catalysts did not have the ability to catalyze the deoxidation reaction of propanediol (or propanol). Therefore, it was reasonable to speculate that 1-PO was generated via the simultaneous cleavage and hydrogenation of two C-O bonds in glycidol. The results of the hydrogenation of propylene oxide gave an irrefutable support for the above suggestion. It was found that mainly propane formed over Co@NG-ZIF (with a 87.0% selectivity at a 95.0% conversion of propylene oxide) (Table S3,† entry 8).

Given the fact that different selectivities to 1-PO were detected over Co@NC, Co/AC, and Co@NG-ZIF in the hydrogenation of glycidol (31.7, 53.6, and 85.9%, respectively), the remaining question is what promoted the simultaneous cleavage and hydrogenation of two C-O bonds in glycidol. First, the morphology of Co/AC and Co@NG-ZIF was characterized in detail by TEM (Fig. S11[†]) and compared with that of Co@NC (Fig. 5). It was found that mainly naked Co NPs formed in the Co/AC catalyst (Fig. S11a and b⁺), while the Co@NG-ZIF catalyst consisted of a thick carbon matrix decorated with graphene shell encapsulated Co NPs (Fig. S11c and d[†]). It seemed that the core-shell structure of Co@NG-ZIF was similar to that of Co@NC (Fig. 5). But XPS analysis further indicated that the content of the N element in Co@NG-ZIF (5.8%) was much higher than that in Co@NC (1.1%, Table S4[†]), demonstrating that much more N atoms were incorporated into the graphene shell in Co@NG-ZIF.

H₂-TPD experiments further disclosed that these structure differences among Co/AC (naked Co NPs), Co@NC (thin carbon film with low content of N (1.1%)) and Co@NG-ZIF (thick graphene shell with high content of N (5.8%)), played a crucial role on the adsorption and activation of H₂ (Fig. 7 and 8). On the surface of those core-shell structured catalysts, it was disclosed that electrons can transfer from the metal core to the graphene shell, which increases the electron density of the graphene surface and therefore promotes the adsorption and activation of reactants on the graphene shell to enhance the catalytic activity.^{58,59} Therefore, we speculated that H2 adsorption over Co@NC and Co@NG-ZIF mainly occurred at the carbon shell outside the Co NPs, rather than on the carbon support. The two weak peaks of Co@NC at 68 and 155 °C could be assigned to the desorption of molecular hydrogen from the thin carbon film



Fig. 7 H_2 -TPD profiles of (a) Co@NC, (b) Co/AC and (c) Co@NG-ZIF catalysts.

outside Co NPs,^{15,16,60,61} and of dissociated hydrogen from small amounts of N atoms doped in this carbon film,⁶² respectively (Fig. 7(a) and 8A). On the surface of Co@NG-ZIF, large amounts of dissociated hydrogen were desorbed at 150 °C (Fig. 7(c)), indicating that the abundant N atoms in the graphene shell greatly boosted the adsorption and activation of H₂ on both the graphene shell and the N atoms in it (Fig. 8C).⁶² As for Co/AC, large amounts of dissociated hydrogen were desorbed from the naked Co NPs at 115 °C (Fig. 7b and 8B).⁶³

The above analysis confirmed that H₂ molecules were excessively adsorbed and dissociated (or activated) into H atoms on the naked Co NPs (in Co/AC)^{64,65} and the N-rich graphene shell outside Co NPs (in Co@NG-ZIF)62 at room temperature. And these highly activated H atoms promoted the simultaneous cleavage and hydrogenation of two C-O bonds in glycidol, thus, giving high selectivity to 1-PO during the hydrogenation of glycidol. Recently, Zeng et al. also disclosed that the N atoms incorporated into Co nanosheets could provide distinct hydrogen adsorption and activation sites to highly boost the catalytic activity toward CO₂ hydrogenation; moreover, the hydrogen species adsorbed on N atoms were more active than those on Co NPs.⁶² Therefore, it was reasonable to conclude that the abundant N atoms in Co@NG-ZIF (5.8%) led to the excessive adsorption and activation of H₂ molecules, providing high hydrogenation activity



Fig. 8 Schematic diagram of H₂ adsorption on different Co catalysts.

but at the cost of the high selectivity of undesired 1-PO in the hydrogenation of glycidol. Similarly, the excessively activated hydrogen species on Co@NG-ZIF also stimulated the simultaneous hydrogenation of two C–O bonds in propylene oxide to propane (Table S3,† entry 8). Meanwhile the thin carbon film outside Co NPs would inhibit the excessive adsorption and activation of H₂ molecules, and the moderate amount of hydrogen species on Co@NC contributed to the selective cleavage and hydrogenation of the C–O bond of neighboring –CH₂ OH to form 1,3-PDO. The conclusion was also confirmed by the hydrogenation of propylene oxide over Co@NC, that is, the C–O bond of neighboring –CH₃ was selectively hydrogenated, and the obtained selectivity to 1-propanol was 86.8% (Table S3,† entry 7).

5 Conclusions

In summary, a carbon film encapsulated Co NP catalyst (Co@NC) was synthesized via the direct pyrolysis of $Co_2(bdc)_2(ted)$ in a N₂ atmosphere. And it was confirmed that Co@NC was highly active, selective and stable for the hydrogenation of glycidol to 1,3-PDO among the tested Pt-, Pd-, Co-, Ni-, Cu- and Ru-based catalysts under mild conditions. The best yield of 1,3-PDO over the Co@NC catalyst reached 50.4% at 140 °C, 2.0 MPa H₂ and 4 h. A series of characterization results disclosed that the carbon film could inhibit the excessive adsorption and activation of H₂ molecules on the naked Co NPs, and a moderate amount of activated hydrogen species on Co@NC contributed to the selective hydrogenation of the C-O bond of neighboring -CH₂OH to form 1,3-PDO. Meanwhile the excessively dissociated H atoms on naked Co NPs (in Co/AC) and abundant N atoms (in Co@NG-ZIF) stimulated the simultaneous cleavage and hydrogenation of both C-O bonds in glycidol to undesired 1-PO.

Conflicts of interest

There are no conflicts to declare.

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