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Multiporous Carbon Encapsulated Ni Nanoparticles Promote Glycerol Valorisation towards Hydrogenation against Rearrangement

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Summary of main observation and conclusion A dual-templating method was used to synthesize a series of hierarchical carbon supports containing ifferent proportions of spherical macropores (*ca.* 200 nm in diameter) and mesoporous channels (*ca.* 4 nm in diameter). These and some other conventional carbon materials were subsequently impregnated with Ni and tested for the conversion of glycerol. The hierarchical catalysts exhibited a significantly higher conversion (96%) and selectivity (77%) to 1,2-propanediol, and the specificity selectivity coefficients (6.1) towards 1,2-propanediol against lactic acid was 'pree times higher than that observed over a conventional Ni/C_{micro} catalyst (2.1). The enhanced performance of these materials, compared with the Ni nanoparticles supported on conventional carbon supports, was attributed to their high surface areas (> 1110 m² g⁻¹) and large pore volumes (*ca.* 0.4 cm³ g⁻¹) remitting greater accessibility of substrate and/or intermediates to Ni active sites. Given that the concentration of accessible Ni sites in these materials is igher, a competitive Benzilic-acid-rearrangement reaction to produce lactic acid was suppressed, leading to an enhanced hydrogenation selectivity to 1,2-propanediol This study evidences the potential benefits which can be established from utilizing hierarchical support materials in the valorization of biomass.

Background and Originality Content

Biomass is considered to be a promising alternative to c nventional fossil-based feedstocks for the production of commodity chemicals and liquid fuels.^[1]

Glycerol is a biomass-derived platform chemical, produced in 1 rge quantities as a by-product from the transesterification of vegetable and animal fats; a key process for the production of 1st generation bio-fuels.^[2] The current global drive to increase uependencies on renewable feedstocks is projected to substantially increase the industrial production of glycerol over the coming y ars.^[3] As such, the catalytic conversion of glycerol into high-value compodity chemicals, such as 1,2-propanediol (PDO), lactic acid (LA)^{cr, 5]} and ethylene glycol (EG),^[6, 7] has been extensively studied and the developments have been documented in a number of views.^[3, 8, 9] Among them, the efficient production of PDO from glycerol can be achieved via developing highly active hydrogenation c talysts.

Supported Ni catalysts are widely acknowledged to be promising hydrogenation catalysts,^[10] but are somewhat limited by tl eir hydrothermal stability.^[11] We have previously reported that pported Ni catalysts are effective for the hydrogenolysis of glycerol. A significant deactivation over subsequent uses was oserved, this is attributable to Ni leaching and particle agglomeration.^[12-15] It was later determined that the deactivation of supported Ni catalysts could be suppressed by adjusting the pH of t¹e reaction solution through the addition of base (e.g. NaOH).^[16] This elegant strategy to stabilize Ni nanoparticles under hydrothermal conditions, was determined to reduce Ni leaching and particle growth via Ostwald ripening at pH >8.[17]

It has been reported that under alkaline conditions, the catalytic selectivity to PDO over supported Ni catalysts is directly related to the rate of hydrogenation of intermediates 2-hydroxyacrolein or pyruvaldehyde over the Ni sites.^[16] As such, we deduce that increasing the accessibility of Ni metal sites would promote the hydrogenation process. Based on conclusions drawn from our previous studies,^[12-16] a reaction scheme is proposed, documenting all the potential reaction pathways which could occur, see Scheme 1. The tandem reaction of glycerol to PDO involves the dehydrogenation of glycerol (1) to glyceraldehyde (GA, 2),^[18] which subsequently undergoes dehydration to produce 2-hydroxyacrolein (HA, 3) or pyruvaldehyde (PA, 4).^[16] The sequential hydrogenation of these intermediates leads to the formation of PDO (5).^[19] It is evident, that the rate of this final hydrogenation reaction influences the reaction selectivity to LA and PDO, as this hydrogenation reaction competes directly with the Benzilic-acid-rearrangement reaction, resulting in the formation of LA (6).^[20] As such, we propose that improving the efficiency of this hydrogenation reaction would indirectly suppress the rearrangement reaction, ultimately promoting the reaction selectivity to PDO.

The use of porous supports has been demonstrated to be highly effective for improving the activity and stability of Ni nanoparticles in the hydrogenolysis of cellulose and xylose.^[21-23] Mesoporosity can contribute to the anchoring of Ni nanoparticles due to channel confinement effects,^[24] which promote the stability of supported Ni catalysts under hydrothermal conditions. It can therefore be postulated that advances in glycerol hydrogenolysis may arise from the application of multifunctional and hierarchical support materials.

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Numerous porous carbon materials, such as carbon nanotubes (CNT),^[25] carbon nanofibers (CNF),^[26] high-surface-area graphite (HSAG)^[27] and graphene oxide (GRO)^[28] have been investigated as both catalysts and supports for the hydrogenolysis of glycerol. However, to date, work in this area has predominantly focused on the synthesis and testing of mesoporous materials and as such, investigation into the potential of using hierarchical materials containing both macro- and mesopores has been somewhat ignored. It is known that macroporous frameworks benefit diffusion process,^[29, 30] leading to increased accessibility of reactants to ternal metal active sites.^[31-33] As such, we reasoned that the application of a hierarchical carbon support, consisting of both eso- and macro-pores, could reduce the reactant/product mass transfer limitations and facilitate greater accessibility to Ni active s tes. This in turn, would increase the rate of the hydrogenation action and ultimately, promote reaction selectivity to PDO. Herein, we describe in detail a method for the synthesis of hierarchical rbon materials, which possess both macropores (200 nm) and well-ordered mesoporous channels (4 nm). These materials were aded with Ni nanoparticles and investigated for the selective hydrogenolysis of glycerol to PDO.



cheme 1 Proposed reaction scheme for the hydrogenolysis of glycerol over Ni supported catalysts under alkaline conditions. 1 - Glycerol, 2 – g vceraldehyde (GA), 3 - 2-hydroxyacrolein (HA), 4 - pyruvaldehyde (PA), - 1,2-propanediol (PDO), 6 - lactic acid (LA), 7 - ethanol, 8 - ethylene glycol (EG), 9 - methanol.

Results and Discussion

ynthesis, characterization and testing of the multiporous carbon catalysts

Macro-mesoporous carbon materials (MMCs) were synthesized by the modification of a dual-templating procedure.^[34] In detail,

polystyrene spheres (PS) and SBA-15 synthesized in-situ from tetraethyl orthosilicate (TEOS), were used as the templating agents of macropores and mesopores, respectively.^[35] The initial composite was prepared by combining TEOS and PS at a weight ratio of 6 (TEOS/PS) in the presence of P123 surfactants. This composite was subsequently calcined to remove the spheres and formed macromesoporous SBA-15 composite. This was then coated in glucose, carbonized and etched to remove the silica template. The final material, denoted as MMC-X (X denotes the ratio of TEOS/PS, herein X = 6), was impregnated with Ni(NO₃)₂·6H₂O, calcined and reduced to yield the final Ni/MMC-6 catalyst (Figure 1a-b). The images from the electron microscopy confirmed that the material did indeed consist of larger Ni nanoparticles (ca. 3-7 nm in diameter) in the macropores (Figure 1a and Figure S2) and a large proportion of Ni nanoparticles (ca. 2-4 nm in diameter) in mesoporous channels (Figure 1b and Figure S2). two additional materials with different proportions of meso- and macro-pores were also synthesized (Figure c and e). This was achieved by changing the ratio of TEOS and PS used in the templating stage of the preparation. For the synthesis of these additional materials, TEOS/PS ratios of 1 and 18 were used; denoted as MMC-1 and MMC-18, respectively.



Figure 1. (a, b) TEM images of Ni/MMC-6 catalyst. (c, d, e) SEM images of MMC materials in the proportion of mesopore to macropore (18, 6, 1).

To further understand how the multipores of the support affected catalytic performance, a number of other carbon supports were also investigated. These included a microporous carbon material (C_{micro}), carbon nanotubes (CNT) and an additional macropore-free mesoporous carbon material (MC). The C_{micro} and MC materials were synthesized using the same templating procedure invoked for the preparation of the MMC-6 catalyst (the absence of templates). All of these carbons were subsequently impregnated with Ni, following the same methodology used for the preparation of the Ni/MMC-6 catalyst.

The textural properties of these carbon catalysts were subsequently investigated by N_2 physisorption, the results of which

are displayed in Table S1 & Figure S2. The measured total surface area and pore volume for each of the Ni/MMC-X materials were found to be substantially higher than those determined for the Ni/C_{micro} and Ni/CNT materials. The surface areas of all the Ni/MMC-X catalysts were all determined to be greater than 1110 $m^2 \cdot g^{-1}$, whereas that of the Ni/C_{micro} and Ni/CNT catalysts were substantially lower (~ 250 $m^2 \cdot g^{-1}$). In addition, the pore volume of all the Ni/MMC-X catalysts (~ 0.4 cm³ \cdot g^{-1}), was determined to be approximately four times higher than that observed for the Ni/C_{micro} and Ni/CNT catalysts (~ 0.1 cm³ \cdot g^{-1}).

The Ni catalysts were subsequently tested for the hydrogenolysis of glycerol under alkaline conditions (20 wt.% glycerol, 0.5 M aOH, 4 MPa H₂, 210 °C, 6 h). The results of these experiments are displayed in Table 1. The presence of macropores in the Ni/MMC-X catalysts had a pronounced effect on the conversion of glycerol. lycerol conversions up to 95 % were observed in the reactions conducted over the Ni/MMC-X catalysts, which was notably higher an that exhibited in the reaction over the macropore-free Ni/MC catalyst (80 %). Lower glycerol conversions were also exhibited by e Ni/Cmicro and Ni/CNT catalysts. The lowest and highest reaction selectivity to PDO was exhibited by the Ni/Cmicro (49.2 %) and Ni/MMC-X (> 76 %) catalysts respectively. The ratio between the eso- and macroporosity in the Ni/MMC-X catalysts did not appear to have an effect on the PDO selectivity (~77 %), but was notably gher than the PDO selectivity observed over the mesoporous Ni/MC (71 %). The selectivity to C₃ products (PDO and LA) was comparable for all the hierarchical catalysts (Ni/MC and Ni/MMC-X) which were tested (~90 %), while the Ni/Cmicro exhibited a lower C₃ selectivity of 73%. Only trace quantities of by-products emanating from further degradation were observed. Interestingly, e ratio between LA and PDO produced over the different catalysts v ried quite significantly. As discussed previously, LA is produced Jy the rearrangement reaction from PA, the reaction of which competes directly with the hydrogenation of PA/HA to produce PDO. Ven that higher PDO selectivity is observed with the Ni/MMC-X catalysts, it indicates that these catalysts are likely to be more efficient hydrogenation catalysts than the other catalysts Investigated. In order to quantify this trend, we have proposed a specificity coefficient (α), defined below:

$$=\frac{\text{Selectivity}_{1,2-\text{PDO}}}{\text{Selectivity}_{LA}}$$
(1)

The α values for the reactions conducted over each of the atalysts are displayed in Table 1. The Ni/MMC-X catalysts exhibited α values between 5.8 – 6.1, which is approximately three ti nes higher than that exhibited by the Ni/C_{micro} catalysts (2.1) and approximately twice higher than that exhibited by the Ni/CNT and Ni/MC catalysts; determined to be 3.4 and 3.9 respectively.



Figure 2 Stability tests of 12.5% Ni/MMC-1 catalyst for the glycerol hydrogenolysis. The pentangle (\star) denotes the specificity coefficient towards hydrogenation to 1,2-propanediol (α). Herein, PDO (1,2-propanediol), LA (lactic acid), EG (ethylene glycol).

The stability of the Ni/MMC-1 catalyst over sequential runs was also investigated and the results from these experiments are displayed in Figure 2 and Table 1. The catalyst was determined to be stable up to at least 4 uses, and only a minor drop in the glycerol conversion and PDO selectivity was observed. This slight drop in activity is likely to be attributed to a reduction in the total surface area of the catalyst, which was determined by BET characterization of the catalyst after a 5th consecutive reaction (Table S2). To verify that this slight deactivation was not attributed to the leaching of Ni species, ICP-OES analysis was conducted on the post-reaction effluent after a standard reaction (210 °C, 6 h) with Ni/MMC-1; only trace quantities (<0.2 ppm) of Ni were observed (<0.8 wt% of initial Ni loading), indicating the small deactivation is not likely to be a result of Ni leaching.

Origin of the improved hydrogenation activity

Reactants and products can readily enter and exit micropores, but usually experience diffusional effects as a consequence. This diffusional limitation will undoubtedly be reduced in the Ni/MMC-X catalysts, as the pore volumes associated with these materials are significantly larger than those of the other conventional carbon supports (Table S1). This would reduce any steric hindrance and mass transfer^[21] across the catalyst and ultimately, improve accessibility to and from the active sites (Ni metal sites or acid sites).^[33] This is one possible explanation as to why a higher reaction activity and selectivity to PDO is observed with the Ni/MMC-X catalysts. An increased accessibility to the Ni sites would likely lead to an increased rate in the hydrogenation of HA (**3**) and PA (**4**). Given that this hydrogenation reaction competes directly with the rearrangement reaction, it can be used to rationalize why higher selectivity to PDO is observed as the expense of LA.

In addition to enhancements in surface area and pore volume, it was also important to consider how the hierarchical MMC materials

Acc

			Conversion [%]	Carbon balance ^[b] [%]	Carbon selectivity [%]				coefficient of
	Entry	Catalyst			PDO	LA	EG	Ethanol	specificity $\alpha = S_{PDO} / S_{LA}$
	1	Raney Ni ^[13]	66.1	85.7	48.4	22.5	4.9	2.5	2.2
	2	Ni/C _{micro}	74.3	86.1	49.2	23.9	6.9	1.3	2.1
	3	Ni/CNT	84.7	93.6	67.4	19.8	3.6	1.7	3.4
	4	Ni/MC	80.9	95.8	71.0	18.4	3.7	1.7	3.9
	5	Ni/MMC-1	94.7	96.4	76.3	14.5	3.7	1.7	5.2
	6	Ni/MMC-6	95.5	95.9	77.1	12.6	4.2	1.8	6.1
	7	Ni/MMC- 18	93.9	96.5	76.6	13.0	5.1	1.6	5.8
	:8	Ni/MMC-1 (4 th run)	87.2	87.9	71.0	12.0	1.7	2.0	5.9
-	9	Ni/MMC- 1(4 th run+ reduced) ^[c]	90.0	92.9	72.0	15.1	3.1	1.9	4.8

 Table 1
 Aqueous-phase hydrogenolysis of glycerol over Ni-based carbon catalysts under alkaline conditions.^[a]

^[a] Reaction conditions: 12.5 wt.% Ni loading, 20 wt.% glycerol, 0.5 M NaOH, wt % (substrate/catalyst) = 8, p (H₂) = 4 MPa, 210 °C, 6 h. Herein, PDO (1,2-propanediol), LA (lactic acid in form of lactate), EG (ethylene glycol).

^[b] Others: methane, methanol, 1-propanol.

^[c] Ni/MMC-1 recycled after the 4th run was then reduced under hydrogen.

arfected the properties of the supported Ni nanoparticles. In order to determine how the support materials affected the redox properties, H₂-TPR experiments were conducted on the calcined catalysts prior to their reduction, see Figure 3. For each of the catalysts investigated, there are two clear reduction peaks present. The peak at proximately 272 °C can be assigned to the reduction of NiO crystals over the macropores or on the external grains of the laterial.^[36] Interestingly, this peak shifts to a higher temperature when an increased proportion of macropores were present in the N/MMC-X materials. Assuming that this ascribes to an increased quantity of large NiO particles present on the surface of the macropores, based on the particle size distributions displayed in gure 1 and S2, we can conclude that the reducibility of the NiO particles decreases as the particle size increases.

Another reduction peak is also observed with all the catalysts at approximately 422 °C. Previous reports have indicated that this peak is indicated to the reduction of NiO particles immobilized on the external or internal surface of mesoporous carbon.^[37] This aligns with the results displayed in Figure 3, as the intensity of this peak is

proportional to the quantity of mesopores present in the calcined materials. The results from the TPR experiments clearly indicate that the properties of the support material have a significant effect on the reducibility of the NiO nanoparticles.

H₂-TPD experiments were subsequently performed, the results of which are displayed in Figure 3. A large desorption peak was observed at approximately 70 °C with all of the materials. The lowest desorption temperatures; exhibited by the hierarchical catalysts (Ni/MMC and Ni/MC), indicates that the bond strength of Ni-H is weaker than the other catalysts, hence the release of hydrogen over Ni particles supported on MMC is more favorable. This could be evidenced as to the greater hydrogenation activity, and as a consequence to a greater PDO selectivity from the Ni-MMC catalysts. From the H₂-TPR and H₂-TPD experiments, we can conclude that the redox properties of the Ni catalysts are heavily influenced by the porosity of the carbon support. Figure 3 H2-TPR profiles for the Ni/MMC catalysts and H2-TPD profiles for Ni/CNT, Ni/Cmicro and Ni/MMC catalysts.

Conclusions

Multiporous carbon supported Ni catalysts are highly active, selective and stable catalysts for the hydrogenolysis of glycerol to PDO. The high performance of these catalysts was predominantly attributed to their high surface areas and pore volumes, which was roposed to reduce mass transfer limitations in the system. The macroporous component in these materials also influenced the edox properties of the supported Ni nanoparticles. H₂-TPD experiments revealed a downward shift in temperature for hydrogen desorption in the Ni/MMC-X catalysts, which was postulated to be result of weaker Ni-H bond strengths. This study is an example of how hierarchical support materials can be used to tailor catalytic ctivity and selectivity in liquid phase reactions.

Experimental

Materials

Styrene (99%, TCI Co., Ltd.), divinylbenzene (80%, Aladdin

silicas as the hard template.^[34] HF (10 wt.% in H_2O) was used to ensure the complete removal of silica template.

Preparation of 12.5 wt.% Ni/MMC catalysts

The Ni catalysts were prepared by an incipient wetness impregnation method.^[41] The support (MC and MMC-X) were immersed in a precursor solution containing Ni(NO₃)₂·6H₂O in deionized water (10 mL). It was followed by vacuum drying at 120 °C for 4 h. All catalysts were subsequently reduced under a flowing 5% H₂/Ar at 300 °C for 2 h (5°C·min⁻¹). The Ni loading (12.5 wt.% Ni) was confirmed by ICP-OES method.

1.3 Catalyst characterization

Powder X-ray diffraction patterns were obtained using a Bruker D8 Advance X-ray powder diffraction instrument with a Cu-Ka radiation (k=0.154 nm, 40 kV and 10 mA,). The ICP-OES was conduct on a ThermoiCAP 6300 spectrometer. Scanning electron microscopy images were collected on a Philips XL-30. BET surface areas were determined by N₂ adsorption-desorption experiments with a Micromeritics ASAP 2020. H₂ temperature programmed



Ltd.), potassium persulfate (99%, Aladdin Co., Ltd.), Tetraethyl orthosilicate (TEOS, Si(OC₂ H₅)₄, SiO₂>28.5%), olyethylene oxide–polypropylene oxide–polyethylene oxide (P123, \pm O20PO70EO20, *M*w = 5800, Sigma-Aldrich Co., Ltd.), Ni(NO₃)₂·6H₂O (A.R., Sinopharm Chemical Reagent Co., Ltd.), lucose (98%, Aladdin Co., Ltd), glycerol (99%, Aladdin Co., Ltd).

1.2 Catalyst preparation

Synthesis of macro-mesoporous carbon

Polystyrene spheres were first prepared by the method proposed y Vaudreuil et al.^[29, 38, 39] Then macro-mesoporous SBA-15 silica composite (MM-SBA15) were prepared via a dual-templating route.^[40] Finally, the macro-mesoporous carbon (MMC-X) was prepared by a modified nano-casting method, which utilized glucose as the carbon precursor and the newly synthetic MM-SBA15-X

reduction and desorption experiments were conducted on a Micromeritics Autochem II 2920 chemisorption instrument.

In a H₂-TPR experiment, catalyst (50~100 mg) was pretreated in air at 150 °C for 1 h to remove physically adsorbed H₂O and other impurities. After cooling to room temperature, the sample was flushed for 0.5 h and then heated to 850 °C at a heating rate of 10 °C·min⁻¹ with a flowing of 5% H₂/Ar (50 cm³·min⁻¹). In a H₂-TPD experiment, catalyst (50~100 mg) was prereduced for 1 h in a flowing 5% H₂/Ar. After cooling to room temperature, the sample was flushed for 0.5 h and then heated to 850 °C at a rate of 10 °C·min⁻¹ with a flowing of Ar (50 cm³·min⁻¹).

1.4 Catalytic reaction

In a standard reaction, catalyst (0.05 g) was reduced in-situ under H_2 at 400 °C for 2 h at a heating rate of 5 °C min⁻¹, and was then transferred to a 50 mL Teflon-lined stainless-steel autoclave.

Report

To this, the reactant solutions (20 wt.% glycerol aqueous solution (10 mL), base additives) were added and the autoclave was sealed. The reactor was then purged with H₂ (2-3 MPa) three times and finally pressurized (4.0 MPa). The reactor was subsequently heated to 210 °C in the oil bath. Upon reaching the desired reaction temperature, the reactor was stirred at 1200 rpm. The reaction was maintained under these conditions for 6 h. Once the reaction was complete, the reactor was cooled down to room temperature by immersing the sealed reactor in icy water. Gas samples were collected with a gas-bag.

1.5 Product analysis

Gas products (Methane) were analyzed by using GC with a mermal conductivity detector (TCD; GC-8A, Shimadzu) equipped with an active carbon column. The liquid-phase products formed in e reaction were quantified by both HPLC and GC-FID (Lactic acid; PDO, EG, EtOH trace amount of methanol and 1-propanol). The "juid phase products (Shimadzu LC-20AB) attached with a refractive index detector (RI, Shimadzu RID 10A) and an Aminex ^LPX-87H column (Bio-Rad, 300×7.8 mm). An aqueous mobile phase containing sulphuric acid (0.005 M) was used at a flow rate of 0.7 mL·min⁻¹. The column temperature was maintained at 60 °C throughout the analysis procedure. The GC-FID was equipped with a polyethylene glycol (PEG) column (20 m \times 0.25 μ m \times 0.25 mm; Palian Zhonghuida Co., Ltd, China). The carbon balance was defined as the percentage of carbon accounted for in the liquid phase after 6 h reaction. The conversion of glycerol was calculated by measuring the amount of glycerol before and after the reaction. The selectivity was calculated by comparing the moles of carbon in the specific product by the moles of carbon in consumed glycerol.

Supporting Information

The supporting information for this article is available on the V/WW under <u>https://doi.org/10.1002/cjoc.2018xxxxx</u>.

Author Contributions

[#]These authors contributed equally to this work.

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Entry for the Table of Contents

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Multiporous Carbon Encapsulated Ni Nanoparticles Promote Glycerol Valorisation towards Hydrogenation against Rearrangement



Ni-based multiporous carbon catalysts containing macropores (~200 nm) and mesoporous channels (~4 nm) are highly selective and stable for glycerol conversion towards the hydrogenation to 1,2-propanediol against rearrangement to lactic acid in alkaline condition.

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