Ni/Co@NDC Modulates the Highly Selective Conversion of Vanillin in Flow Reactor under Mild Conditions

Shanshan Lin[a,c], Jianguo Liu [b*], Lungang Chen [b], Xinghua Zhang [b], Qi Zhang[b], Longlong Ma[b]

[a] CAS Key Laboratory of Renewable Energy, Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, P. R. China.

[b] Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, PR China.

c University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

* Corresponding author: liujg@seu.edu.cn

ABSTRACT

Vanillin is currently the most abundant aromatic molecule produced from lignin on an industrial scale and one of the few renewable resources that can be readily catalyzed to obtain alkanes. The hydrogenation of vanillin as a lignin model has been a hot research topic in the catalytic community. Vanillin has the potential to be upgraded to value-added compounds by catalytic hydrogenation, and its valuable hydrogenation products are usually vanillinol (VA) and 4-methylguaiacol (MMP). The difficulty of this reaction lies in the selectivity control of the hydrogenation products. Complete conversion of both products cannot be achieved with either noble or non-precious metal catalysts in the same catalytic system. For the hydrogenation of vanillin, the usual catalysts can achieve complete conversion of one product or partial conversion of both products. In our work, we developed a novel bimetallic catalyst encapsulated in nitrogen-rich carbon to achieve, for the first time, the selective and regulated conversion of two products, i.e., 96.06% vanillin and 99.99% MMP, in the same system. The use of nitrogen-doped carbon (NDC) as a carrier for Ni nanoparticles allows the charge transfer from Ni to the carrier, i.e., NDC, resulting in the oxidation potential is corrected. Combined with the more favorable deoxidation activity of Co, our catalysts are inexpensive, simple to prepare, stable in performance, easy to separate, high in activity, and have the advantage of being tunable to the target product. Due to the synergistic effect of Ni and Co bimetals, the vanillin hydrogenation reaction can be almost completely stopped at the step of VA generation and the catalytic activity of the active center can be adjusted by controlling the temperature in a continuous flow to achieve the conversion of the other

product MMP at 99.99%, which has never been reported before.

KEYWORD

Vanillin; Vanillyl alcohol; MMP; Heterogeneous catalyst; Flow Reactor

INTRODUCTION

Catalytic transfer hydrogenation (CTH) is considered to be a promising technology for upgrading biomass into fuels and valuable chemicals in the presence of multiphase catalysts [1]. Lignin accounts for 10 - 35 % by weight and up to 40 % of the energy in biomass feedstocks [2],As one of the lignocellulosic biomass fractions can be used directly in the production of alkanes [3, 4]. Vanillin is currently the most abundant aromatic molecule produced on an industrial scale from lignin, and is one of the few renewable resources that can be easily catalyzed to obtain alkanes[5]. The hydrogenation of vanillin as a lignin model has been a hot topic of research in the catalysis community.[6] Vanillin has the potential to be upgraded to value-added compounds by catalytic hydrogenation and its valuable hydrogenation products are typically vanillyl alcohol (VA) and 4-methyl guaiacol (MMP). During the subsequent processing of bio-oils, thermally unstable compounds such as aldehydes, acids and sugars tend to cause catalyst coking and need to be converted to stable compounds (e.g. alcohols and diols).[7].These alcohols are more conducive to the subsequent processing of bio-oils with increased hydrogen content [8].Vanillyl alcohol is also more costly and expensive to produce than vanillin and can be used directly as a flavouring [9].MMMP can be used as a fuel additive or food flavouring agent[10],and is also widely used as an intermediate for flavours or drugs and fragrances[11].The difficulty in this reaction is the selectivity control of the hydrogenation products. The catalysts typically used for the reduction of vanillin are divided into two main categories, noble metals and transition metals. The usual noble metal catalysts （Au[12], Ru[13], Pd[14]） due to their excellent catalytic reduction ability, will strip off O in one step during the reaction to produce 4-methyl guaiacol (MMP). The noble metal catalyst Pd has excellent hydrodeoxygenation ability for vanillin, e.g. Pd@CN N[15] can produce more than 99% MMP under relatively mild

conditions, and up to 97% MMP selectivity when Al2O3 is used as a carrier. [16] A number of noble metals based on C materials (Pt,Pd,Au,Ru,Rh) were used to study the comparative hydrogenation activity towards vanillin.[17] At 100 °C and 3 MPa, Pd/C showed the highest catalytic activity, reaching 95% MMP selectivity at complete conversion. A selective conversion of 93.6% MMP could also be achieved when Pd was catalyzed in concert with the transition metal Cu.[18] However, it is difficult to stay at the step of converting the carbonyl group to the hydroxyl group, i.e. the selective conversion of vanillyl alcohol cannot be achieved. The very few studies with noble metal Ir have only been able to produce up to 54 mol% VA at 25 °C and up to 24 mol% MMP at 50 °C. [19] In addition to the high cost of noble metals, researchers have been working to develop new catalysts such as transition metal catalysts with a higher probability of H2 adhesion and the ability of transition metals to activate hydrogen. The common transition metal catalysts face problems such as harsh reaction conditions, metal leaching and poor environmental tolerance of the carrier. [20] Transition metals such as Ni[1],Cu[21, 22],Co[23, 24] are commonly used as catalytically active centres for HDO catalysts. Ni activity is low compared to noble metals and only 64.6% MMP selectivity can be achieved with NCB as a carrier and is accompanied by by-product formation [25]. However, neither catalyst can achieve complete conversion of each of the two products in the same catalytic system. For the hydrogenation of vanillin, the usual catalysts can achieve complete conversion of one product or achieve partial conversion of both products with modulation [26, 27]. In our work, we have developed a novel bimetallic catalyst encapsulated in nitrogen-rich carbon to achieve, for the first time, the selective and regulated conversion of two products, 96.06% vanillyl alcohol and 99.99% MMP, in the same system. Carbonaceous materials are known to be stable under harsh hydrothermal conditions (350-550 °C) [28]. In addition, the electrochemical properties of carbon materials can be tuned by doping with the heteroatom N[29] Thus, the use of nitrogen-doped carbon (NDC) as a carrier for Ni nanoparticles allows the transfer of charge from Ni to the carrier, i.e. NDC, resulting in a more positive oxidation potential for Ni. Plus Co is more conducive to deoxygenation activity [30], Our catalysts

are therefore inexpensive, simple to prepare, stable, easy to separate and highly active, and at the same time have the advantage of being tunable to the target product. Due to the synergistic effect of Ni and Co bimetals, the vanillin hydrogenation reaction can be almost completely stopped at the intermediate step (**Fig. 1**) to produce VA, and the catalytic activity of the active centre can be regulated by controlling the temperature only to achieve a complete conversion of the other product MMP which has never been reported before.
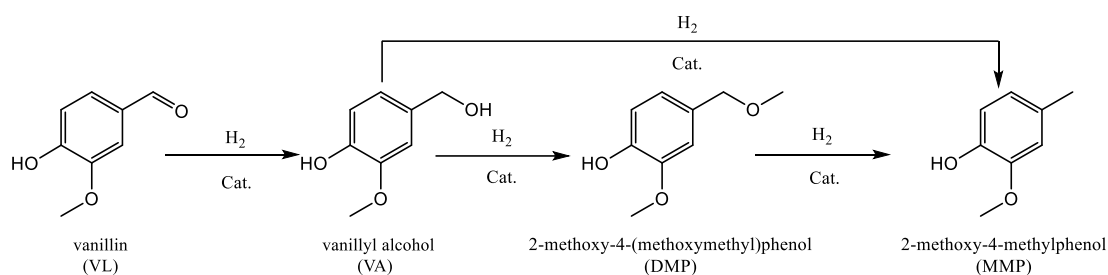

Figure 1. A brief diagram of the stepwise hydrogenation of vanillin

Studies of vanillin hydrogenation in the mobile phase are even less common, as this requires a catalyst with excellent stability and long-lasting activity under tolerant environmental conditions. Based on our previous studies of similar carriers in continuous flow[31],we decided to carry out a vanillin hydrogenation study in a continuous flow system. The development of non-homogeneous catalysts for continuous flow systems facilitates industrial-scale applications as the process of utilising biomass platform compounds requires that they can be operated at long cycle times and on a large scale. [32] In addition, the control of material and temperature, etc., guaranteed by the flow process allows for tunability of the reaction products [33, 34].The flow system can monitor and control the reaction process in real time, start or stop the reaction at any time, and can add raw materials during the reaction process and adjust the flow rate to control the reaction time, which is a flexible, controllable, convenient and efficient reaction system .[35-37] The flow reactor can react the liquid material after gasification in contact with the loaded catalyst, and the reaction efficiency can be significantly improved. Moreover, because the system is fully mixed in multiple phases, local under-hydrogenation is avoided and by-product generation is reduced while improving efficiency.[38, 39] However, this flow system is not without challenges; solid

blockages in small size channels and multiphase mixing may affect or even stop the desired reaction altogether. Therefore, the catalyst in this flow system must be as low as possible in terms of metal loss and ensure high recovery. Therefore, the preparation of new catalysts and the optimization of flow conditions have become indispensable challenges in the development of flow reactor hydrogenation. This work describes a simple and environmentally friendly method to prepare transition bimetallic catalysts Ni/Co@NDC for the selective conversion of vanillin. The catalyst uses transition metals as the active catalytic center, which greatly reduces the preparation cost, and the resulting catalyst is stable and reusable. The reaction was carried out under very mild conditions requiring only 3 bar hydrogen pressure and only a change in reaction temperature to selectively convert readily available lignin platform compounds to VA or MMP at a flow rate of 0.2 mL/min in a highly efficient flow reactor system, thus providing a viable pathway for the low-cost utilization of lignin platform compounds. To prevent small catalyst particles from clogging the flow reactor tube, we adsorbed the magnetic Ni/Co@NDC catalyst onto a magnetic stir bar to leave space for liquid flow. The selective conversion of vanillin was carried out continuously in the flow reactor under optimized conditions with ethanol as the solvent (the product was easily separated), and the conversion and selectivity were excellent.

2. EXPERIMENTAL SECTION

2.1 Materials

$Ni(NO_3)_2 \cdot 6 H_2O$ (AR, 98%), $(CH_3 COO)2 Co$ (AR, 98%)anhydrous citric acid (AR, ≥99.5%), Melamine (AR, 99%),Vanillin (AR, ≥99.0%), vanillyl alcohol (AR, ≥99.0%), 2-Methyl-4-guaiacol (AR, ≥99.0%) was obtained from Shanghai Macklin Biochemical Co., Ltd.; $H2SO4$ (GR, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd.; Methanol (AR, ≥99.7%), dioxane (AR, ≥99.0%), acetonitrile (AR, ≥99.0%), ethanol (AR, 99.7%) were purchased from Aladdin (Shanghai) Chemical Technology Co., Ltd.; Deionized water (σ <5 µS/m) was self-made in the laboratory. Before using, the purity of Vanillin, vanillyl alcohol and 2-Methyl-4-guaiacol has been checked.

2.2 Preparation of Ni/Co@NDC catalysts

Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6\,H_2O$, 0.03 mol), Cobalt acetate ((CH_3COO)2 Co, 0.01 mol), melamine (C3H6N6, 0.03 mol) and citric acid ($C_6H_8O_7$, 0.03 mol) were dissolved in 80 mL of anhydrous ethanol, and then the mixture was stirred at 70 ºC (300 rpm) Aging for 4-8 hours until a pink suspensions is obtained. Place it in a drying oven at 100 ºC for 24 to 72 hours to remove excess water. Then the pink solid obtained was calcined in a fixed bed at 600 ºC under 40 mL min^{-1} of high-purity N_2 (99.999%) atmosphere for 3 h to reduce the catalyst, and the heating rate was controlled at 2 ºC min^{-1}. The resulting black solid was treated in a 1M H_2SO_4 aqueous solution at 70 °C until the solution became colorless to remove unsafe and uncovered Ni ang Co particles. Then, the black solid was washed thoroughly with deionized water until the pH value of the waste liquid was 7. Finally, the black solid was dried in a freeze dryer at -48 ºC for 12 h to obtain the Ni/Co@NDC catalysts.

2.3 Hydrogenation of acetophenone in a flow reactor

The reaction was carried out in a flow reactor (Ou Shisheng (Beijing) Technology Co., Ltd.). First, the flow reactor reaction tube was filled with magnets that could adsorb 100 mg of catalyst to make sure that the thickness of the catalyst on each magnet is about 1mm, and the reaction tube was maintained at a specific reaction temperature (the temperature is detected by the thermocouple in the reactor) and H_2 pressure. Then, the vanillin reaction raw material with a concentration of 0.083 mol/L was passed through. The flow rate of N_2 is 60 mL/min, and the flow rate of H_2 hydrogen is 40 mL/min. The mixed liquid was pumped into the reaction tube made by 316L stainless steel with a length of 200mm and an inner diameter of 6mm at a flow rate of 0.4ml/min, and the reacted mixed liquid flowed through the gas-liquid separator at a constant flow rate and entered the product collection device for Gas Chromatograph measurement. The reaction product was identified by GC and the yield of the reaction product was determined by GC.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterizations of Ni/Co@NDC catalysts

As shown in **Figure 2a**, the c-nanotube structure of the catalyst is clearly visible, with a small amount of graphene spherical shell encapsulated catalyst particles, while the

carbon nanotube structure is almost completely lost in the cycled catalyst (**Fig. 2b**), replaced by graphene spherical shell encapsulated metal The catalysts were replaced by metal nanoparticles encapsulated by graphene spherical shells, but still uniformly distributed. It is assumed that the change in catalyst activity is due to the change in catalyst structure.
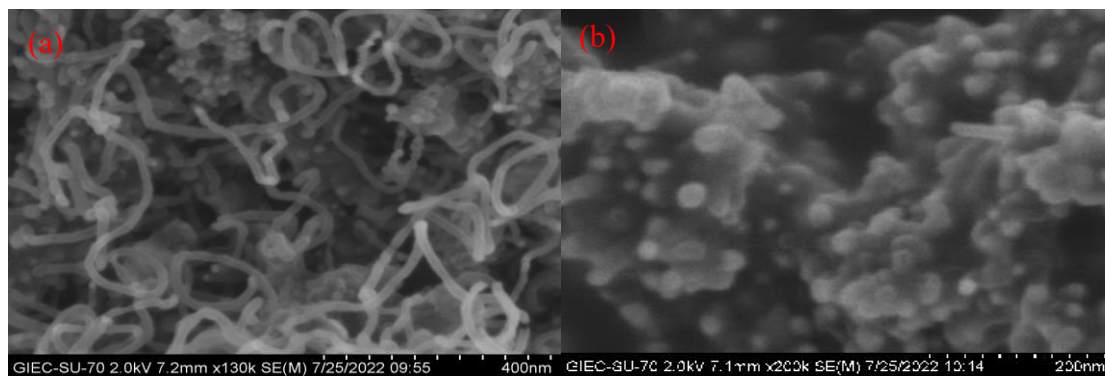

Figure 2. Representative SEM images of (**a**), Ni/Co@NDC (**b**), Ni/Co@NDC (recycled).

Further high resolution (HR) TEM analysis showed that the nanospheres consisted of metallic nanoparticles (NPs) that were completely coated with a graphene shell (**Fig. 3a, 3b**). The d-spacing of the Ni/Co@NDC metal nanoparticles is 0.20 nm, corresponding to the (111) plane of the nickel alloy (**Fig. 3a**). Statistical analysis by high resolution transmission electron microscopy (HR-TEM) showed that the graphene shells on the Ni/Co nanoparticles are very thin, with >90% of the C-shell consisting of a few layers. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images with subÅ resolution further confirm that homogeneous metal nanoparticles have been formed (**Fig. 3c**), and the corresponding energy dispersive X-ray (EDX) maps indicate that N and O atoms are uniformly distributed over all NPs (**Fig. 3c-h**).
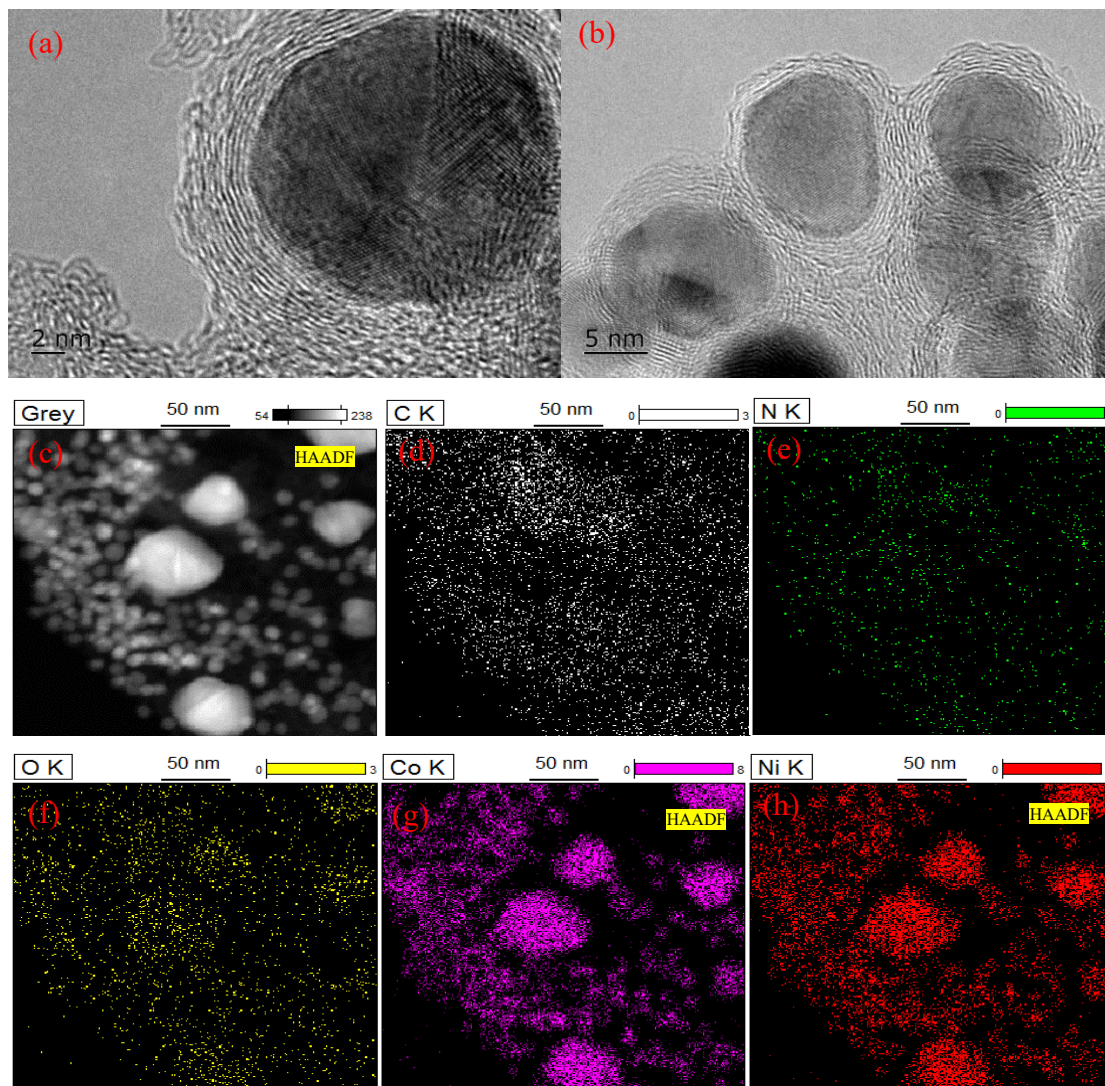
Figure 3. Catalyst characterization. HRTEM images of Ni@C-700-EtOH (a, b). Inset in (a) shows the selected-area electron diffraction pattern. HAADF-TEM images of a single particle in Ni/Co@NDC (c) and corresponding EDS element mapping (EFTEM) of C, N, O, and HAADF-STEM analysis of Ni and Co (d-h).

X-ray diffraction (XRD) was used to investigate the electronic and structural properties of Ni/Co@NDC. The XRD spectrum (**Figure 4**) shows a graphitic carbon shell C(002) between 20 and 30, which confirms the formation of a thin graphene shell. However, the characteristic peaks of Co metal were not found in the XRD spectrum, presumably creating an alloy structure with Co. The XRD peak position of the catalyst did not change after cycling, but the peak signal was slightly weakened, which may be related to the slight metal loss from the catalyst after cycling. These results show that the homogeneous Ni/Co nano-alloys are fully encapsulated in the thin graphene shells. It

can be seen that the metal is evenly distributed in the catalyst particles and that each catalyst particle is uniformly encapsulated by the C shell.
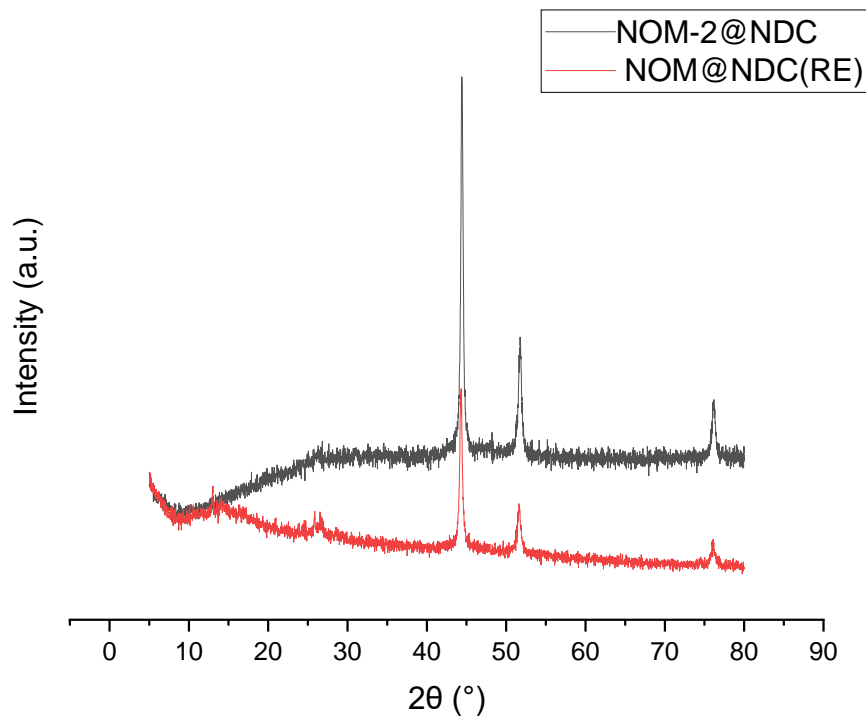

Figure 4. XRD images of Ni/Co@NDC catalyst

3.2 Conversion of vanillin using Ni/Co@NDC catalysts in the flow reactor

The schematic diagram of the Ni/Co@NDC catalyst conversion of vanillin in a flow reactor is shown in **Figure 5**.
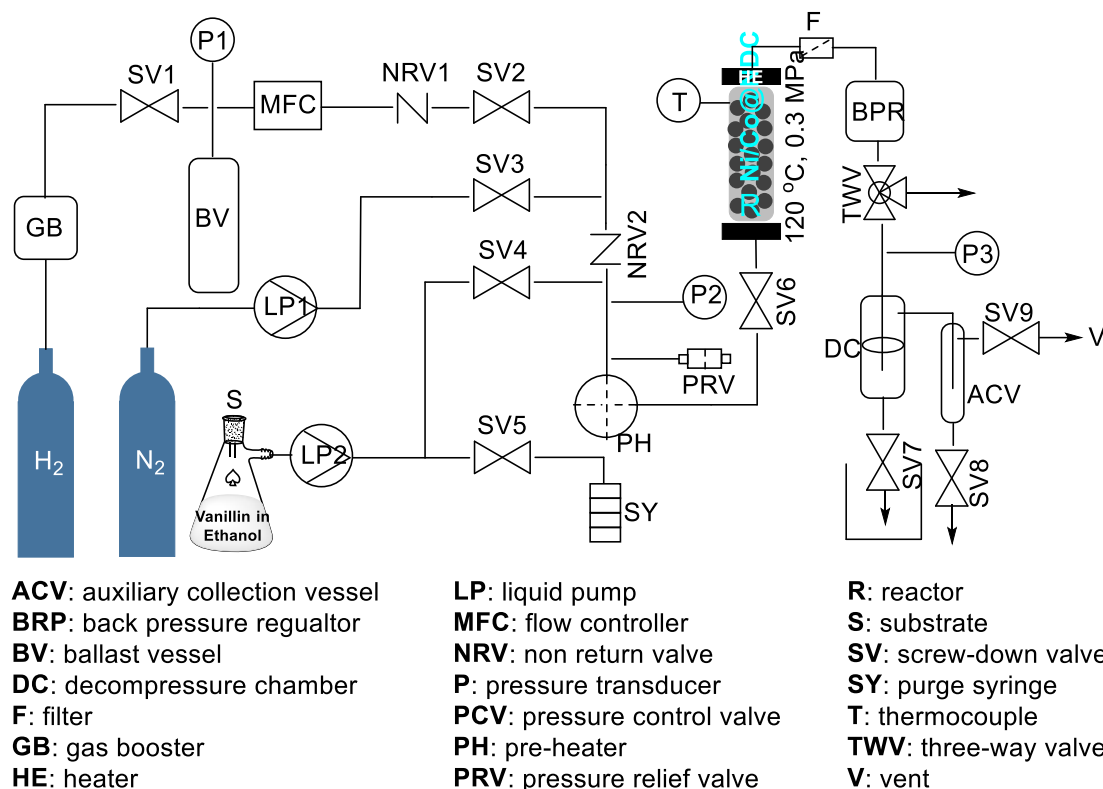
ACV: auxiliary collection vessel
BRP: back pressure regualtor
BV: ballast vessel
DC: decompressure chamber
F: filter
GB: gas booster
HE: heater

LP: liquid pump
MFC: flow controller
NRV: non return valve
P: pressure transducer
PCV: pressure control valve
PH: pre-heater
PRV: pressure relief valve

R: reactor
S: substrate
SV: screw-down valve
SY: purge syringe
T: thermocouple
TWV: three-way valve
V: vent

Figure 5. Schematic drawing of the pipeline structure of the flow reactor for Ni/Co@NDC catalyzed reduction of vanillin.

We first tested the effect of the catalyst on the hydrogenation of vanillin in a methanol solvent (Table 1, Entry 1) in batch reactor and found that although the selectivity for VA was high, the reaction produced DMP by-products, presumably due to the involvement of methanol. We then reran the reaction in a methanol solvent at a reduced reaction temperature (Table 1, Entry 2) and chose two other solvents (Table 1, Entry 3, 4) that did not contain active hydroxyl groups to test if the by-product formation could be reduced and the reaction would stay in the conversion to VA, but apparently the results were not as expected at low temperatures. We proceeded to restore the reaction temperature and chose ethanol, a solvent less polar than methanol but more soluble in hydrogen[40] , and achieved a VA selectivity of 95.11 without any by-products (Table 1, Entry 5). We then transferred the reaction system to a continuous stream and used the excellent mass and heat transfer properties of the continuous stream for subsequent screening of the conditions.

Table 1. The results of the temperature and solvent effect in THR of vanillin in batch reactor.

Entry[a]	Temp. [°C]	Solv.	Conv. [%]	VA Sel. [%]	MMP Sel. [%]
1	100	MeOH	99.99	71.49	-
2	50	MeOH	95.79	-	-
3	50	1,4-Dioxane	27.01	-	-
4	50	ACN	-	-	-
6	100	ACN	60.33	3.22	-
5	100	EtOH	70.65	95.11	4.89

a) Reaction conditions: vanillin, 0.5 mmol; solvent, 6 mL; 5 mg Ni/Co@NDC catalyst; reaction pressure, 1 MPa; reaction time, 4 h.

As shown in Figure 6a, the conversion reached over 99.99% with increasing temperature. Interestingly, at a reaction temperature of 100 °C, the selectivity of VA reached 96.06%, while a further increase of 20 °C resulted in the conversion of all VL to MMP. In the pressure screening process (Fig. 6 b), we found that at a hydrogen pressure of 3 bar, VA could still achieve more than 99.99% MMP selectivity, which is a very mild reaction condition in our known previous studies. However, we found that the reaction required a certain reaction time. As shown in Figure 6 c, during the flow rate screening process, not only did the conversion decrease significantly with increasing flow rate, but also the selectivity of both VA and MMP decreased. The decrease in MMP selectivity with reaction time and the peak-shaped change in VA selectivity are due to the fact that during the hydrogenation of VL, VA is first hydrogenated to produce VA and then VA continues to be hydrogenated to produce MMP, so the shorter reaction time is more favourable to the production of VA. After a long screening run, the optimized conditions were used for a 15 h continuous experiment without catalyst replacement (Fig. 6 d). The experimental results show that the catalyst has a certain degree of deactivation. The ICP results show that the Co content of the original NOM@NDC catalyst is 44.38%, the Ni content is 20.36%, and the ratio between metals is 2.17. The Co content of the recycled catalyst is 35.48 %, the Ni content was 16.27%, and the metal ratio was 2.18. It indicated that the catalyst after

cycling had a slight loss of metal in the same proportion. Since the catalyst metal was not seriously lost, we suspected that the deactivation phenomenon was related to the change of the catalyst structure.
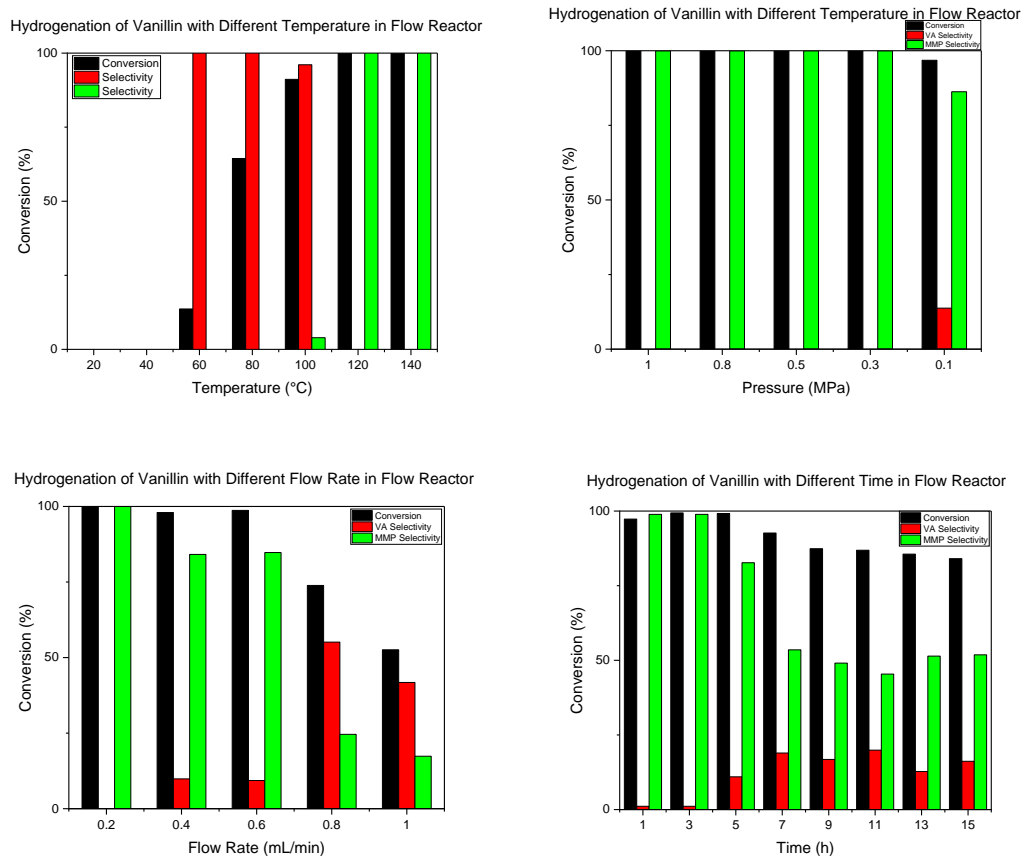

Figure 6. Study of reaction factors for the Ni/Co@NDC catalyzed reduction of vanillin to Vanilla alcohol in a flow reactor. Reaction conditions: (a) Reaction conditions: 1 g catalyst Ni/Co@NDC, 0.083 mol/L vanillin (solvent: EtOH), 1 MPa H_2, different reaction temperature, 0.2 mL/min; (b) Reaction conditions: 1 g catalyst Ni/Co@NDC, 0.1 mol/L vanillin (solvent: EtOH), different H_2 pressure, 120 °C, 0.2 mL/min; (c) Reaction conditions: 1 g catalyst Ni/Co@NDC, 0.1 mol/L vanillin (solvent: EtOH), 1 MPa H_2, 120°C, different flow rate; (d) Reaction conditions: 1 g catalyst Ni/Co@NDC, 0.1 mol/L vanillin (solvent: EtOH), 1 MPa H_2, 120 °C, 0.2 mL/min. Conversion and selectivity were determined by GC.
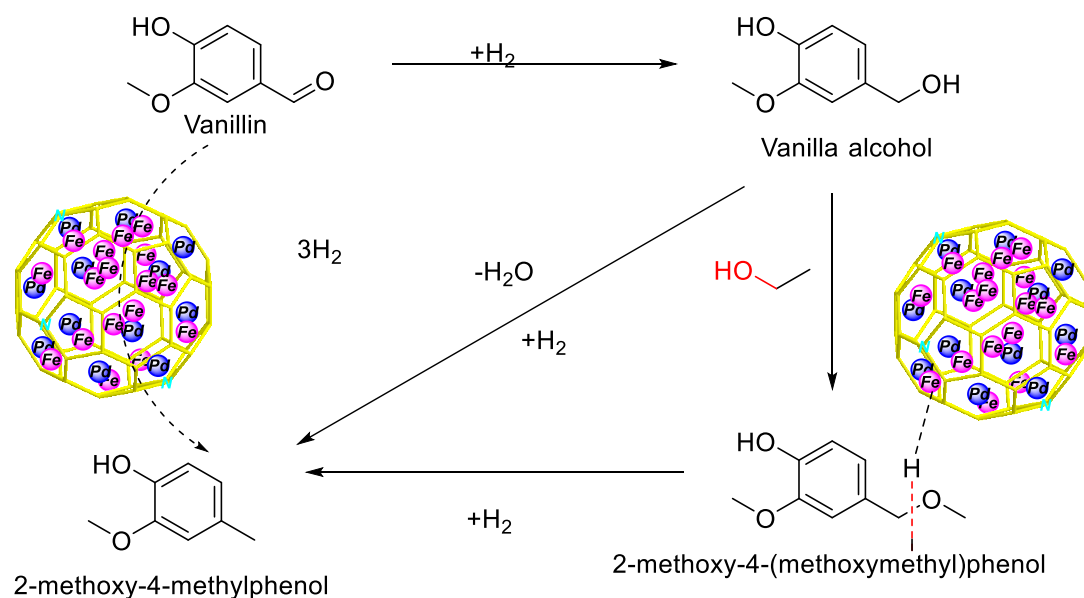
Figure 7. Proposed mechanism of Ni/Co@NDC catalyzed hydrogenation of vanillin to vanillyl alcohol or MMP.

First, the substrate is adsorbed onto the catalyst active material and the C-O bond is activated and broken with the help of Ni/Co-H substances. Then it is hydrogenated to hydroxyl groups to produce vanillin (VA). VA can be hydrogenated in one step to produce MMP, or it can be reacted with ethanol to produce a DMP intermediate, which removes the CH3OH added in the previous step and is hydrogenated again to produce MMP. if the reaction conditions are too mild or the reaction time is not sufficient, the reaction will stay in the DMP step and produce by-products.

CONCLUSION.

In conclusion, we have developed a bimetallic catalyst loaded on NDC for the hydrogenation of vanillin in a continuous flow, achieving for the first time the selective and regulated conversion of both products (VA, MMP) in the same system. The catalyst is simple to prepare, low cost, high activity and stable performance. the interactions between the two metals Ni, Co can regulate the selective conversion of vanillin very precisely. By exploiting the excellent mass and heat transfer properties of continuous flow, the reaction conversion can reach 99.99%.

AUTHOR CONTRIBUTIONS J. G. L. supervised and designed the research. S.S.L. performed the experiments and data analysis. S.S.L. and J. G. L. co-wrote the original

manuscript. J.G.L. reviewed and corrected the manuscript. All authors discussed the results and assisted during manuscript preparation.

COMPETING INTERESTS The authors declare no competing financial interests.

DATA AVAILABILITY Data supporting the findings of this study are available from the corresponding authors upon reasonable request.

ADDITIONAL INFORMATION Correspondence and requests for materials should be addressed to J. G. L. or L. L. M.

REFERENCES

1   Li G. T., Li H. Enhancing Activity of Ni2P-Based Catalysts by a Yolk-Shell Structure and Transition Metal-Doping for Catalytic Transfer Hydrogenation of Vanillin. Energ Fuel 2021; 35 (5): 4158-4168.doi:10.1021/acs.energyfuels.0c03771

2   Jin W., Pastor-Perez L., Shen D. K. et al. Catalytic Upgrading of Biomass Model Compounds: Novel Approaches and Lessons Learnt from Traditional Hydrodeoxygenation - a Review. Chemcatchem 2019; 11 (3): 924-960.doi:10.1002/cctc.201801722

3   Parsell T. H., Owen B. C., Klein I. et al. Cleavage and hydrodeoxygenation (HDO) of C-O bonds relevant to lignin conversion using Pd/Zn synergistic catalysis. Chem Sci 2013; 4 (2): 806-813.doi:10.1039/c2sc21657d

4   Schutyser W., Renders T., Van D. et al. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chemical Society Reviews 2018: 852

5   Fache M., Boutevin B., Caillol S. Vanillin Production from Lignin and Its Use as a Renewable Chemical. Acs Sustain Chem Eng 2016; 4 (1): 35-46.doi:10.1021/acssuschemeng.5b01344

6   Thijs V., Wouter S., Tom R. et al. Perspective on Lignin Oxidation: Advances, Challenges, and Future Directions. Topics in Current Chemistry 2018; 376 (4): 30

7   Bindwal A. B., Vaidya P. D. Reaction Kinetics of Vanillin Hydrogenation in Aqueous Solutions Using a Ru/C Catalyst. Energ Fuel 2014; 28 (5): 3357-3362.doi:10.1021/ef500498z

8   Huber G. W., Cortright R. D., Dumesic J. A. Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates. Angew Chem Int Edit 2004; 43 (12): 1549-1551.doi:10.1002/anie.200353050

9   Liguori F., Moreno-Marrodan C., Barbaro P. Biomass-derived chemical substitutes for bisphenol A: recent advancements in catalytic synthesis. Chemical Society Reviews 2020; 49 (17): 6329-6363.doi:10.1039/d0cs00179a

10   Meylemans H. A., Groshens T. J., Harvey B. G. Synthesis of Renewable Bisphenols from Creosol. Chemsuschem 2012; 5

11   Sylvain, Caillol, Maxence et al. Vanillin Production from Lignin and Its Use as a Renewable Chemical. Acs Sustain Chem Eng 2016

12   Yang X. M., Liang Y., Zhao X. et al. Au/CNTs catalyst for highly selective hydrodeoxygenation of vanillin at the water/oil interface. Rsc Adv 2014; 4 (60): 31932-31936.doi:10.1039/c4ra04692g

13   Yang X., Liang Y., Cheng Y. et al. Hydrodeoxygenation of vanillin over carbon nanotube-

supported Ru catalysts assembled at the interfaces of emulsion droplets. Catalysis Communications 2014; 47: 28–31

14   Crossley S., Faria J., Shen M. et al. Solid Nanoparticles that Catalyze Biofuel Upgrade Reactions at the Water/Oil Interface. Science 2010; 327 (5961): 68-72.doi:10.1126/science.1180769

15   Xu X., Li Y., Gong Y. T. et al. Synthesis of Palladium Nanoparticles Supported on Mesoporous N-Doped Carbon and Their Catalytic Ability for Biofuel Upgrade. J Am Chem Soc 2012; 134 (41): 16987-16990.doi:10.1021/ja308139s

16   Hao P. X., Schwartz D. K., Medlin J. W. Phosphonic acid promotion of supported Pd catalysts for low temperature vanillin hydrodeoxygenation in ethanol. Appl Catal a-Gen 2018; 561: 1-6.doi:10.1016/j.apcata.2018.05.008

17   Santos J. L., Alda-Onggar M., Fedorov V. et al. Hydrodeoxygenation of vanillin over carbon supported metal catalysts. Applied Catalysis A: General 2018: 137-149

18   Shit S. C., Singuru R., Pollastri S. et al. Cu-Pd bimetallic nanoalloy anchored on a N-rich porous organic polymer for high-performance hydrodeoxygenation of biomass-derived vanillin. Catal Sci Technol 2018; 8 (8): 2195-2210.doi:10.1039/c8cy00325d

19   Smith C. A., Brandi F., Al-Naji M. et al. Resin-supported iridium complex for low-temperature vanillin hydrogenation using formic acid in water. Rsc Adv 2021; 11 (26): 15835-15840.doi:10.1039/d1ra01460a

20   Sadaba I., Granados M. L., Riisager A. et al. Deactivation of solid catalysts in liquid media: the case of leaching of active sites in biomass conversion reactions. Green Chem 2015; 17 (8): 4133-4145.doi:10.1039/c5gc00804b

21   Petitjean, Gagne, Beach et al. Highly selective hydrogenation and hydrogenolysis using a copper-doped porous metal oxide catalyst. Green Chem 2016

22   Fan R. Y., Chen C., Han M. M. et al. Highly Dispersed Copper Nanoparticles Supported on Activated Carbon as an Efficient Catalyst for Selective Reduction of Vanillin. Small 2018; 14 (36).doi:ARTN 180195310.1002/smll.201801953

23   Liu G. L., Robertson A. W., Li M. M. J. et al. MoS2 monolayer catalyst doped with isolated Co atoms for the hydrodeoxygenation reaction. Nat Chem 2017; 9 (8): 810-816.doi:10.1038/Nchem.2740

24   Shit S. C., Koley P., Joseph B. et al. Porous Organic Polymer-Driven Evolution of High-Performance Cobalt Phosphide Hybrid Nanosheets as Vanillin Hydrodeoxygenation Catalyst. Acs Appl Mater Inter 2019; 11 (27): 24140-24153.doi:10.1021/acsami.9b06789

25   Nie R. F., Yang H. H., Zhang H. F. et al. Mild-temperature hydrodeoxygenation of vanillin over porous nitrogen-doped carbon black supported nickel nanoparticles. Green Chem 2017; 19 (13): 3126-3134.doi:10.1039/c7gc00531h

26   Mahfud F. H., Bussemaker S., Kooi B. J. et al. The application of water-soluble ruthenium catalysts for the hydrogenation of the dichloromethane soluble fraction of fast pyrolysis oil and related model compounds in a two phase aqueous-organic system. J Mol Catal a-Chem 2007; 277 (1-2): 127-136.doi:10.1016/j.molcata.2007.07.004

27   Busetto L., Fabbri D., Mazzoni R. et al. Application of the Shvo catalyst in homogeneous hydrogenation of bio-oil obtained from pyrolysis of white poplar: New mild upgrading conditions. Fuel 2011; 90 (3): 1197-1207.doi:10.1016/j.fuel.2010.10.036

28   Adam, H., Van et al. Stability of functionalized activated carbon in hot liquid water. Carbon

2014

29   Monte F. D., Gutierrez M. C., Lopez-Salas N. et al. Nitrogen-doped carbons prepared from eutectic mixtures as metal-free oxygen reduction catalysts. Journal of Materials Chemistry A 2015: 478-488

30   Tran N. T. T., Uemura Y., Chowdhury S. et al. Vapor-phase hydrodeoxygenation of guaiacol on Al-MCM-41 supported Ni and Co catalysts. Appl Catal a-Gen 2016; 512: 93-100.doi:10.1016/j.apcata.2015.12.021

31   Lin S. S., Liu J. G., Ma L. L. Ni@C catalyzed hydrogenation of acetophenone to phenylethanol under industrial mild conditions in a flow reactor. React Chem Eng 2022; 7 (5): 1126-1135.doi:10.1039/d1re00513h

32   Gérardy R., Debecker D. P., Estager J. et al. Continuous Flow Upgrading of Selected C 2 − C 6 Platform Chemicals Derived from Biomass. Chemical Reviews 2020; 120 (15)

33   Continuous Flow Organic Chemistry: Successes and Pitfalls at the Interface with Current Societal Challenges. European Journal of Organic Chemistry 2018; 2018 (20-21)

34   Hommes A., Heeres H. J., Yue J. Catalytic Transformation of Biomass Derivatives to Value-Added Chemicals and Fuels in Continuous Flow Microreactors. Chemcatchem 2019 (11-19)

35   Yoshida J., Takahashi Y., Nagaki A. Flash chemistry: flow chemistry that cannot be done in batch. Chem Commun 2013; 49 (85): 9896-9904.doi:10.1039/c3cc44709j

36   Wiles C., Watts P. Continuous flow reactors: a perspective. Green Chem 2012; 14 (1): 38-54.doi:10.1039/c1gc16022b

37   Hartman R. L., McMullen J. P., Jensen K. F. Deciding Whether To Go with the Flow: Evaluating the Merits of Flow Reactors for Synthesis. Angew Chem Int Edit 2011; 50 (33): 7502-7519.doi:10.1002/anie.201004637

38   Ley S. V., Baxendale I. R. New tools and concepts for modern organic synthesis. Nat Rev Drug Discov 2002; 1 (8): 573-586.doi:10.1038/nrd871

39   Geyer K., Codee J. D. C., Seeberger P. H. Microreactors as tools for synthetic chemists - The chemists' round-bottomed flask of the 21st century? Chem-Eur J 2006; 12 (33): 8434-8442.doi:10.1002/chem.200600596

40   d'Angelo J. V. H., Francesconi A. Z. Gas-liquid solubility of hydrogen in n-alcohols (1 <= n <= 4) at pressures from 3.6 MPa to 10 MPa and temperatures from 298.15 K to 525.15 K. J Chem Eng Data 2001; 46 (3): 671-674.doi:DOI 10.1021/je000189u