

Conversion of Biomass into H₂-rich Syngas and Metal-graphene-nanotube
Multifunctional Hybrid Materials for Use in Field-emitter Devices and
Double-layer Capacitors: An Innovative Hypothetical Approach



Table of content

- 3 Conversion of Biomass into H₂-rich Syngas and Metal-graphene-nanotube Multifunctional Hybrid Materials for Use in Field-emitter Devices and Double-layer Capacitors: An Innovative Hypothetical Approach

Conversion of Biomass into H₂-rich Syngas and Metal-graphene-nanotube Multifunctional Hybrid Materials for Use in Field-emitter Devices and Double-layer Capacitors: An Innovative Hypothetical Approach

Atef Sobhy Iskander

Catalytic conversion of lignocellulosic biomass into H₂-rich syngas or high-value chemicals is considered sustainable alternatives to those derived from petrochemical refineries and related fossil fuel transformations. This conversion process is a great challenging target due to the complex reaction routes and the associated problems arising from purification and separation processes. Herein, an innovative hypothetical approach is proposed for the conversion of biomass into high quality H₂-rich syngas and three-dimensional metal-graphene-nanotube multifunctional hybrid materials for use in field-emitter devices and double-layer capacitors. Concerning the gasification of biomass, a two-successive stage process is proposed, namely *ex situ* and *in situ* process, in which steam is used as the gasifying agent under an inert atmosphere. In *ex situ* process, a magnetic CoFe₂O₄ nanoparticles@ ZSM-5 zeolites would be employed as a catalyst to allow a partial upgrading process, which would enhance the Brønsted acidity, exhibiting a high selectivity of aromatics and olefins as well as suppression coke formation and reduction the impurities. Using a magnet, the catalyst can be recovered for reuse. In *in-situ* process, further treatment of the products of the former phase would be accomplished *via* a different catalytic route using Fe/Al₂O₃ deposited on graphene/porous nickel film as a catalyst at a high temperature. The expected role of this system would lead to obtaining a high-quality of H₂-rich syngas; and producing the target metal-graphene-nanotube materials. The synergetic effect of this hybrid catalyst would significantly improve both the yields of gases and the hydrogenation of aromatics. These new efficient catalytic routes can be adapted in industrial-scale processes, providing a creative idea and reference for energy supplement development and high-value chemicals production.

Keywords: Biomass, Syngas, Gasification, Acid-Functionalized Magnetic Nanoparticles, Carbon Nanotubes.

1. Introduction

Energy derived from plant biomass is considered one of the most important sustainable alternatives to those derived from fossil fuel. Plant biomass is the most abundant renewable resource available and has the potential to overcome the problems arising from depletion of fossil fuels and global warming issues. Lignocellulosic biomass comprises a complex mixture of three major components, *i.e.*, cellulose (30-50 wt%), hemicellulose (20-35 wt%), and lignin (15-30 wt%)¹. Cellulose contains glucose as a sole sugar unit, whereas hemicellulose is a heterogeneous molecular compound composed of a range of polysaccharides, such as xylan, glucuronoxylan, and glucomannan. Lignin is an amorphous, polyphenolic material arising from an enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers, coniferyl, synapyl and *p*-coumaryl alcohols. Lignin is the most abundant aromatic biopolymer accounting for up to 30% of the organic carbon on Earth and thus can be treated as a potential renewable feedstock for energy supplement and aromatic chemicals production.^{2,3}

Thermal conversion of lignocellulosic biomass, especially fast pyrolysis, has shown great promise in producing added-value chemicals and fuels as sustainable alternatives to those derived from petrochemical refineries and related fossil fuel transformations. Indeed, the distinctive and chemical characteristics of biomass offer a potential avenue to be energy resource, produce high-value chemicals, reduce landfills and slow global warming. However, thermal degradation is a complex process through which biomass particles simultaneously undergo many different reactions, such as dehydration, depolymerization, fragmentation, and carbonization, producing liquid oil, char residues, and gaseous products.^{4,5} In reality, conversion of biomass by thermochemical process has been employed to produce gaseous fuels, primarily H₂, CO, and CH₄.⁶ In this process, carbonaceous feedstock was converted into gaseous fuel in the presence of a certain amount of oxidants, such as O₂, air, steam, and CO₂ at a relatively higher temperature. Biomass gasification can produce H₂-rich flammable gas with high thermal efficiency. Hydrogen energy is one of renewable energy that is distinguished by feature of high energy density, odorless, non-toxic, and zero pollution. Generally, generation of synthesis gas can be achieved by different processes among them gasification reforming of biomass, which can be either processed to produce fuel combined with chemicals *via* Fischer-Tropsch process, or purified to produce H₂-rich syngas. In fact, gasification is a two-step process, *i.e.*, the first step is devolatilization, in which the pyrolysis of solid biomass feedstock in the presence of a gasifying agent, such as steam, CO₂, H₂, etc. produces non-condensable gas (H₂, CO, CO₂, and hydrocarbons), condensable volatiles (liquid oil), and solid char, while the second step is the reforming of volatiles in the gas phase. However, this gasification technology suffers from the contamination of syngas with gaseous oil (a complex mixture of condensable organic compounds), which results in chemical energy loss in syngas, soot formation, poisoning of catalysts, and the decrease of overall energy efficiency.⁷⁻⁹ In addition, this thermochemical process contains traces of impurities, such as H₂S, COS, NH₃, HCN, and alkali metals, which are associated with their negative impact on the process and the environment.

To overcome these challenges, a wide range of catalytic reforming methods have been employed during the process of biomass gasification to eliminate the gaseous oil through selected bond cleavage reactions, such as deoxygenation, cracking, decarbonylation, and other reactions.^{8,10-12} In fact, gasification is the most effective method to convert low-quality resources to syngas (a mixture of H₂ and CO), which its quality depends on the gas composition and heating value. In the reforming process, the compositions of H₂-rich gas can be affected by a gasifying agent, the feedstock, and the catalyst (such as mineral catalysts, metal-based catalysts,

partial zeolites, and activated char-based catalyst).¹³ Syngas produced by biomass gasification has a wide industrial and commercial application ranging from H₂ generation, fuel production, heat and power generation, to the synthesis of methanol and bio-based products.^{14,15} However, although many effective catalytic reforming processes have been developed for gasification technology and efficient removal of oil from syngas on a laboratory scale, these catalysts are not optimally productive in industrial-scale processes, and the quality of bio-oil obtained from biomass pyrolysis is still a primary concern.¹⁶⁻¹⁸ Moreover, the purification and separation of the products resulting from pyrolysis of biomass are another burdensome process. Herein, I propose an innovative hypothetical approach for the conversion of biomass into high quality H₂-rich syngas and three-dimensional metal-graphene-nanotube multifunctional hybrid materials for use in field-emitter devices and double-layer capacitors.

2. The proposed approach

Searching for an optimal catalytic system for the gasification process, the following requirements should be taken into consideration: i) reducing the activation energy of the cracking reaction, ii) enhancing the formation of CO and H₂ in the syngas *via* the water-gas shift reaction (WGSR) with a minimum amount of gasifying agent, iii) the selective and targeted realization of the catalytic conversion of biomass,¹⁹ and iv) economic viability.

In view of these demands, the proposed process is divided into two successive stages using steam as the gasifying agent under an inert atmosphere (N₂ or Ar atmosphere). Each stage is characterized by its novel multifunctional catalyst under optimized process conditions. First, the catalytic process would be performed in *ex situ* system using a magnetic ZSM-5 nanoparticle as a catalyst. Second, *in situ* process, the product of the first phase would be subjected to a metal-graphene multifunctional hybrid material as a catalyst at a high temperature.

2.1. The objectives of this approach

This hypothetical approach has a dual objective: i) to increase hydrogen production and gas yield through upgrading the vapor-phase bio-oil effectively, so that these gases can be further used as feedstock for liquid fuels or fuel cells; and ii) to produce selective chemicals, *i.e.* metal-graphene-nanotube multifunctional hybrid materials, capitalizing on the high aromatic content and reaction conditions during the gasification process. These metal-graphene-nanotube multifunctional hybrid materials have a wide application especially for use in field-emitter devices and double-layer capacitors.

2.2. The expected results of this hypothetical approach and discussion

2.2.1. The two-phase gasification process

The aim of performing the two-stage gasification process is to accurately predict product yields during

biomass pyrolysis and to define a well-shaped model, which takes into account primary and secondary reactions during the pyrolysis process. In the primary phase, biomass would be thermally degraded into solid products (carbon and chars), liquid products (tars, and hydrocarbons), and gas products (CO, CO₂, H₂O, C₂₋₆H_x). In the secondary phase, the intermediate tars and char resulting from the primary reactions would be further cracked to yield syngas and activated carbon (Figure 1).^{20,21}

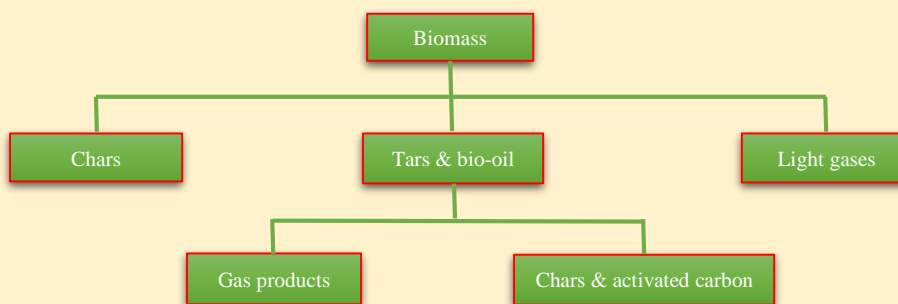


Figure 1. Two-stage scheme for the biomass pyrolysis processes.

One of the most important factors that control the molecular reactions of biomass during the pyrolysis process, is the heat/mass transfer. These reactions could be classified into: i) biomass moisture losses at temperatures below 100 °C; ii) primary phase pyrolysis at 200-600 °C, in which biomass decomposes into the solid, liquid, and non-condensable gas products; and iii) secondary phase pyrolysis at 300-800 °C, in which large molecules are cracked to produce gases and bio-oil.²² Generally, the increased reactor temperature would result in the high yields of H₂ and CO, while the yields of bio-oil and char would be decreased.

The integrated multifunctional catalysts would allow the process to be performed at atmospheric pressure without other additional reactive agents or harsh conditions. Furthermore, the advantage of performing the *ex situ* pyrolysis process of biomass is to augment bio-oil yield by mitigating biomass's mineral matter as well as to reduce particles' moisture and oxygen contents, resulting in improved energy efficiency and product quality. Another feature, the flexibility of *ex situ* configuration would allow for a less complex process, and pave the way for the integration of the next catalytic phase.

2.2.2. The gasifying agent & inert atmospheres

The conducted steam as a gasifying agent during the pyrolysis of solid feedstock would improve the composition and heat value of the syngas product through enhancing the formation of CO and H₂ in the syngas through WGS reaction (Eq. 1). In addition, catalytic reforming under inert atmospheres would guarantee the formation of H₂ and CO as the major components, as well as produce a large amount of syngas (especially CO) at a relatively process conditions.

Water-gas shift (WGS) reaction: C_nH_m (gaseous oil) + $H_2 \longrightarrow CO + H_2 + CH_4 + \dots + \text{cock}$ (1)

2.2.3. The expected role of magnetic ZSM-5 nanoparticles in *ex situ* phase

The aim of performing this stage in *ex situ* phase is: i) to provide a high aromatic/olefins yields; ii) to allow an optimum catalyst performance at an optimized reaction temperature and residence time; iii) to remove the impurities; and iv) to recover the catalyst for reuse.

The proposed magnetic ZSM-5 nanoparticles are magnetic $CoFe_2O_4$ -embedded ZSM-5 zeolites nanoparticles. Deoxygenation of bio-oil is a crucial step, which would result in a higher value of transport fuel product due to a higher aromatic content. Thus, the deoxygenation and upgrading process can be flexibly performed in an environment independent of that required for pyrolysis, which would allow to achieve a partial upgrading process under optimum catalyst performance to obtain the high-value products at the optimized conditions.²³ Using ZSM-5 as a medium-pore zeolite would provide a high aromatic yields.²⁴ Furthermore, the incorporation of metal catalysts with ZSM-5 zeolite could achieve excellent cooperative effects for the hydrogenation of aromatics.²⁵ Besides, HZSM-5 has excellent denitrification properties, especially when co-catalyzed with cobalt, which has the ability to enhance the conversion of the undesired volatile N and N-containing compounds to NH_3 , as well as the ability to crack the C-C bonds of nitrile impurities.

Towards an optimal efficiency of the catalyst, the introduction of bimetallic oxides, *i.e.* $CoFe_2O_4$ nanoparticles, would lead to mediate the strong Brønsted acidity, which would display a high selectivity of aromatics and olefins resulting in decomposition of tar and promotion of H_2 and CO_2 formation.²⁶

Due to the nanoscale morphology, Fe/Co nanoparticles-modified ZSM-5 could have the ability to eliminate diffusion restrictions for large molecules, creating complementary active acid sites (as hierarchical pores), which could result in a higher lifetime of zeolite as a result of lower coke formation. Several studies reported that Fe/Co metal species, among other metals, suppress coke formation by tuning the density and activity of acidic sites to a certain extent.^{26,27}

On the other hand, the introduction of magnetic $CoFe_2O_4$ -embedded ZSM-5 nanoparticles would enable to recover the catalyst using a magnet, *e.g.* neodymium magnet, for reuse.²⁸

2.2.4. The expected role of metal-graphene multifunctional hybrid materials in *in-situ* phase

The *in situ* phase is a successive stage of the first *ex situ* phase, in which the product of the first step would be subjected to Fe/ Al_2O_3 deposited on graphene/porous nickel film (metal-graphene multifunctional hybrid materials) as a catalyst at a high temperature (*e.g.* 750 °C). The purpose of this process is to obtain a high-quality of H_2 -rich syngas; and to maximize gaseous oil conversion to produce three-dimensional metal-graphene-nanotube multifunctional hybrid materials.

In fact, the using of this catalyst is mainly to produce added-value carbon nanotube (CNT) forests capitalizing on the aromatic/olefin contents as the carbon source to grow carbon nanotubes under condition similar to that of the preparation of these hybrid materials, *i.e.* at the same reaction temperature (750 °C), and

introducing water during the CNT-growth process to remove amorphous carbon (Figure 2).²⁹ This catalyst contains graphene, which its molecular functionalization can be achieved covalently and non-covalently. In the case of covalent bonds between graphene and a target molecule (*e.g. via* nucleophilic, cycloaddition, condensation, and electrophilic reactions), graphene's π -orbitals are involved in the bond, transforming sp^2 into sp^3 bonds, resulting in changing its electronic transport properties. On the other hand, noncovalent functionalization provides the opportunity of attaching functional groups to the graphene surface based on electrostatic interactions such as van der Waals forces or π - π interactions. Aromatic contents arising from gasification process would be ideal candidates for this purpose, since they can be easily anchored to graphene surface through π - π interactions. Such noncovalent interactions would not alter the conjugated network of graphene, thus preserving its intrinsic properties. However, the CNT forests were found to raise the Fe/ Al_2O_3 catalyst layer during the growth process while the vertically grown CNTs connect to the graphene layer through covalent bonds, resulting in seamless high-quality CNT-graphene-metal interfaces.³⁰

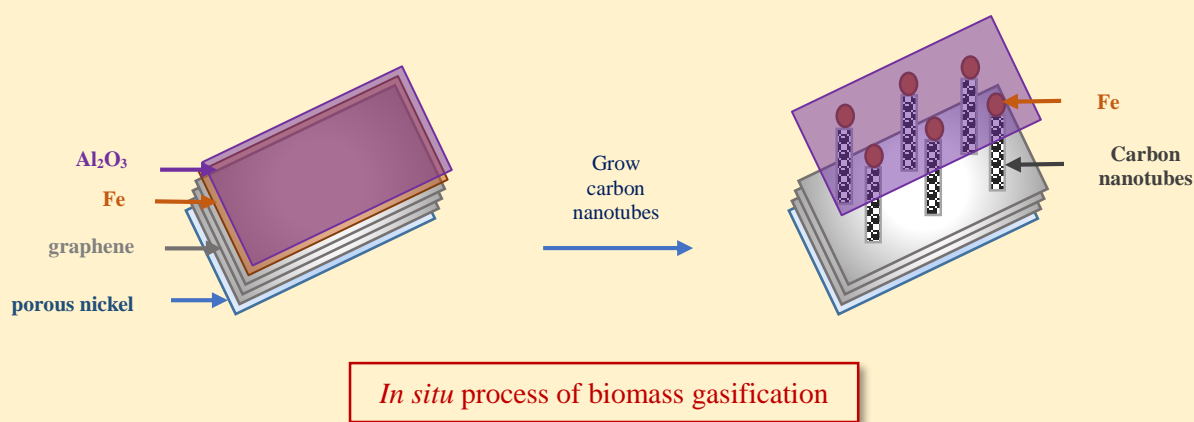


Figure 2. Schematic diagram of the growth of carbon nanotube forests from the graphene surface on porous nickel substrate during gasification reforming while raising the Fe/ Al_2O_3 catalyst layer.

The three-dimensional metal-graphene-nanotube multifunctional hybrid materials can be used in field-emitter devices and double-layer capacitors. Moreover, the produced carbon nanotubes can be employed in several applications such as high performance thermoelectric materials owing to their narrow bandgap energy and high charge carrier mobility. Besides, they can be integrated into flexible thermoelectrics that can cover any waste heat, as well as serving as carbon nanotubes-metal-electrode contacts.

This multifunctional hybrid catalyst would make it possible to produce different phenolic and olefinic compounds, as well as aromatic hydrocarbons, which can further serve as biofuels and bio-chemicals. The incorporating nickel in the catalyst would reduce tar yield and any oxygen content of the bio-oil increasing hydrogen production and gas yield.^{31,32} Ni is an active species for efficient cracking oil during gasification process as well as the ability to promote decomposition of NH_3 .³³ The inclusion of Ni, Fe, and

Al_2O_3 in this multifunctional hybrid catalyst in addition to the graphene would effectively lead to cracking of large organic molecules into smaller molecules at reforming temperature as well as inhibiting coke formation due to the synergetic effect of this hybrid catalyst, enhancing significantly the yields of gases (H_2 , CO , and CH_4) and the hydrogenation of aromatics (increasing selectively the yields of some products).

I hypothesize that these processes would improve the catalytic performance of the conversion of biomass gasification with high selectivity of the desired products and minimizing coke generation in a low-cost technique. In addition, this new efficient catalytic reforming of biomass gasification can be adapted in industrial-scale processes.

3. The proposed synthetic procedures of the catalysts

3.1. The proposed synthetic procedure of the magnetic ZSM-5 nanoparticles catalyst

ZSM-5 zeolite-functionalized magnetic nanoparticles could be prepared in a two-step procedure.^{34,35} First, magnetic CoFe_2O_4 nanoparticles (MNPs) can be synthesized using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and sodium dodecyl sulfate (SDS) in the presence of methylamine (CH_3NH_2). After dispersion of MNPs in ethanol solution, a mixture of isopropanol ($(\text{CH}_3)_2\text{CHOH}$) and water would be added to the solution with sonication. Second, a homogeneous solution of ZSM-5 zeolite in isopropanol would be added to the uniform dispersed solution of MNPs in the presence of aqueous NH_3 with sonication. After washing and drying, the zeolite-coated magnetic nanoparticles would be obtained (Figure 3).

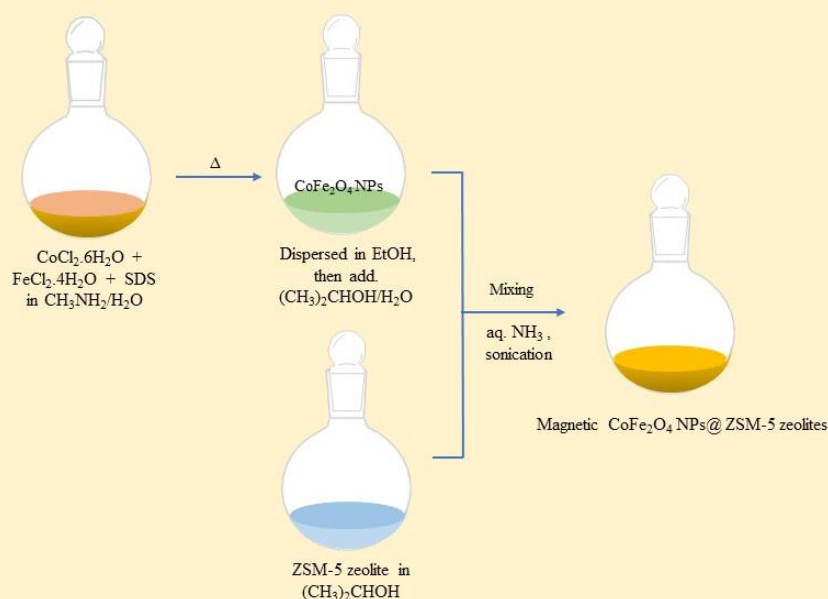


Figure 3. Schematic diagram of the proposed synthesis of magnetic CoFe_2O_4 nanoparticles@ZSM-5 zeolites.

2.2. The proposed synthetic procedure of the metal-graphene multifunctional hybrid materials

The proposed metal-graphene multifunctional hybrid materials could be synthesized according to Yan *et al.*²⁹ In short, a multi-layer graphene would be grown on a foam-like 1.2 mm thick porous nickel films using a chemical vapor deposition method.³⁶ A 1.5 nm thick layer of catalytic Fe would be deposited on the surface of the graphene using e-beam evaporation, followed by the deposition of a 10 nm thick Al_2O_3 as the buffer layer to ensure the catalytic activity of the Fe (Figure 4). The $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst layer would be deposited on both sides of the porous nickel films to increase the amount of carbon nanotubes attached to the substrates during the gasification process.

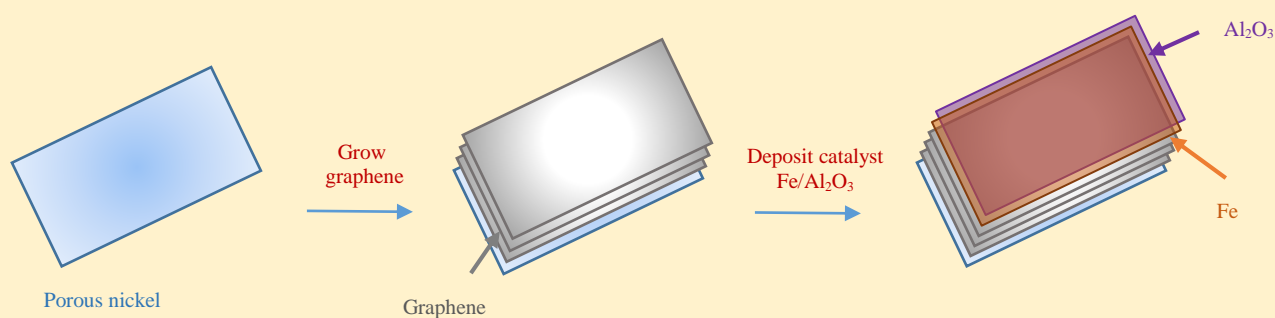


Figure 4. Schematic diagram of the synthesis of the metal-graphene multifunctional hybrid materials.

7. Conclusions

The challenges associated with the purification and separation of the products resulting from the conversion of lignocellulosic biomass into H_2 -rich syngas or high-value chemicals are a major bottleneck in the integration of pyrolysis technique into industrial-scale process. An innovative hypothetical approach is proposed for the conversion of biomass into high quality H_2 -rich syngas and three-dimensional metal-graphene-nanotube multifunctional hybrid materials for use in field-emitter devices and double-layer capacitors. This proposal provides a two-successive stage process for the gasification of biomass, namely *ex situ* and *in situ* process, in which steam is used as the gasifying agent under an inert atmosphere (N_2 or Ar atmosphere). Each stage has its new multifunctional catalytic route under optimized process conditions. In *ex situ* process, a magnetic CoFe_2O_4 nanoparticles @ ZSM-5 zeolites would be employed as a catalyst to allow a partial upgrading process leading to high-value products. Furthermore, this catalyst has the ability to enhance the Brønsted acidity, which would exhibit a high selectivity of aromatics and olefins resulting in

decomposition of tar and promotion of H₂ and CO₂ formation, as well as suppression coke formation and reduction the impurities. Another advantage, the catalyst can be recovered for reuse using a magnet such as a neodymium magnet.

In *in-situ* process, further treatment of the products of the former phase would be accomplished *via* a different catalytic route using Fe/Al₂O₃ deposited on graphene/porous nickel film as a metal-graphene multifunctional hybrid catalyst at a high temperature. The expected role of this system would lead to obtaining a high-quality of H₂-rich syngas; and producing three-dimensional metal-graphene-nanotube multifunctional hybrid materials. The synergetic effect of this hybrid catalyst would significantly improve both the yields of gases (H₂, CO, and CH₄) and the hydrogenation of aromatics.

This contribution would improve the catalytic performance of the conversion of biomass gasification with high selectivity of the desired products in a low-cost technique. In addition, these new efficient catalytic routes can be adapted in industrial-scale processes, providing a creative idea and reference for energy supplement development and high-value chemicals production.

References

- 1) J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, *Green Chemistry*, **2014**, *16*, 4816–4838.
- 2) B. M. Upton, A. M. Kasko, *Chemical Reviews*, **2016**, *116*, 2275–2306.
- 3) C. Xia, L. Cai, H. Zhang, L. Zuo, S. Q. Shi, S. S. Lam, *Biofuel Research Journal*, **2021**, *29*, 1296–1315.
- 4) P. R. Patwardhan, C. R. Brown, B. H. Shanks, *ChemSusChem.*, **2011**, *4*, 636–643.
- 5) P. R. Patwardhan, J. A. Satrio, R. C. Brown, B. H. Shanks, *J. Anal. Appl. Pyrolysis.*, **2011**, *86*, 323–330.
- 6) M. Inayat, S. A. Sulaiman, J. C. Kurnia, M. Shahbaz, *Renewable Sustainable Energy Rev.*, **2019**, *105*, 252–267.
- 7) D. A. Bulushev, J. R. H. Ross, *Catal. Today*, **2011**, *171*, 1–13.
- 8) X-Y. Ren, X-B. Feng, J-P. Cao, W. Tang, Z-H. Wang, Z. Yang, J-P. Zhao, L-Y. Zhang, Y-J. Wang, X-Y. Zhao, *Energy Fuels*, **2020**, *34*, 10307–10363.
- 9) S. Y. Liu, D. H. Mei, L. Wang, X. Tu, *Chem. Eng. J.*, **2017**, *307*, 793–802.
- 10) J. Feroso, P. Pizarro, J. M. Coronado, D. P. Serrano, *WIREs. Energy Environ.*, **2017**, *6*, e245.
- 11) I. Graca, J. M. Lopes, H. S. Cerqueira, M. F. Ribeiro, *Ind. Eng. Chem. Res.*, **2013**, *52*, 275–287.
- 12) X. C. Qian, G. Z. Bai, P. P. He, Z. Y. Fei, Q. Liu, Z. X. Zhang, X. Chen, J. H. Tang, M. F. Cui, X. Qiao, *Ind. Eng. Chem. Res.*, **2018**, *57*, 16875–16883.
- 13) J. Ren, Y. L. Liu, X. Y. Zhao, J. P. Cao, *J. Energy Inst.*, **2020**, *93*, 1083–1098.
- 14) L. J. Wang, C. L. Weller, D. D. Jones, M. A. Hanna, *Biomass Bioenergy*, **2008**, *32*, 573–581.
- 15) S. Sartipi, K. Parashar, M. J. Valero-Romero, V. P. Santos, B. Van Der Linden, M. Makkee, F. Kapteijn, J. Gascon, *J. Catal.*, **2013**, *305*, 179–190.
- 16) S-H. Kong, S. S. Lam, P. N. Y. Yek, R. K. Liew, N. L. Ma, M. S. Osman, C. C. Wong, *J. Chem. Technol. Biotechnol.*, **2019**, *94*, 1397–1405.
- 17) S. S. Lam, X. Y. Lee, W. L. Nam, X. Y. Phang, R. K. Liew, P. N. Yek, Y. L. Ho, N. L. Ma, M. H. Rosli, *J. Chem. Technol. Biotechnol.*, **2019**, *94*, 1406–1415.
- 18) S. S. Lam, M. H. Su, W. L. Nam, D. S. Thoo, C. M. Ng, R. K. Liew, P. N. Yek, N. L. Ma, V. D. V. Nguyen, *Ind. Eng. Chem. Res.*, **2019**, *58*, 695–703.
- 19) J. Ren, X.-P. Cao, X.-Y. Zhao, F.-L. Yang, X.-Y. Wei, *Energy Rev.*, **2019**, *116*, 109426.
- 20) K. Papadikis, S. Gu, A. V. Bridgwater, *Chem. Eng. J.*, **2009**, *149*, 417–427.
- 21) C. Xia, S. Q. Shi, *Green Chem.*, **2016**, *18*, 2063–2071.
- 22) R. S. Miller, J. Bellan, *Combust. Sci. Technol.*, **1996**, *119*, 331–373.
- 23) L. J. Xu, Y. Zhang, Y. Fu, *Energy Technology*, **2017**, *5*, 30–51.
- 24) J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo, G. W. Huber, *J. Catal.*, **2011**, *279*, 257–268.

- 25) Y. Tang, W. J. Yu, L. Y. Mo, H. Lou, X. M. Zheng, *Energy Fuels*, **2008**, *22*, 3484–3488.
- 26) P. R. Bhoi, A. S. Ouedraogo, V. Soloiu, R. Quirino, *Renewable Sustainable Energy Rev.*, **2020**, *121*, 109676.
- 27) R. N. Liu, M. M. Rahman, M. Sarker, M. Chai, C. Li, J. Cai, *Fuel Process. Technol.*, **2020**, *199*, 106301.
- 28) A. Takagaki, M. Nishimura, S. Nishimura, K. Ebitani, *Chem. Lett.*, **2011**, *40*, 1195-1197.
- 29) Z. Yan, L. Ma, Y. Zhu, I. Lahiri, M. G. Hahm, Z. Liu, S. Yang, C. Xiang, W. Lu, Z. Peng, Z. Sun, C. Kittrell, J. Lou, W. Choi, P. M. Ajayan, J. M. Tour, *ACS Nano*, **2013**, *7*, 58-64.
- 30) Y. Zhu, L. Li, C. Zhang, G. Casillas, Z. Sun, Z. Yan, G. Ruan, Z. Peng, A-R. O. Raji, C. Kittrell, R. H. Hauge, J. M. Tour, *Nat. Commun.*, **2012**, 10.1038/ncomms2234.
- 31) Z. Ma, V. Custodis, J. A. van Bokhoven, *Catal. Sci. Technol.*, **2014**, *4*, 766-772.
- 32) J. Geng, W. L. Wang, Y. X. Yu, J. M. Chang, L. P. Cai, S. Q. Shi, *Bioresour. Technol.*, **2017**, *227*, 1-6.
- 33) N. Abdoulmoumine, S. Adhikari, A. Kulkarni, S. A. Chattanathan, *Appl. Energy*, **2015**, *155*, 294–307.
- 34) C. S. Gill, B. A. Price, C. W. Jones, *J. Catal.*, **2007**, *251*, 145-152.
- 35) A. J. Rondinone, A. C. S. Samia, Z. J. Zhang, *J. Phys. Chem. B*, **1999**, *103*, 6876-6880.
- 36) Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H. M. Cheng, *Nat. Mater.*, **2011**, *10*, 424–428.