

Hydrogen Production from Catalytic Formic Acid Decomposition over Zn Based Catalysts under Room Temperature

(Penghasilan Hidrogen daripada Penguraian Bermangkin Asid Formik Menggunakan Mangkin Berasaskan Zn pada Suhu Bilik)

Masitah Abdul Halim Azizi^{a,*}, Wan Nor Roslam Wan Isahak^a, Norliza Dzakaria^b & Mohd Ambar Yarmo^b

^aResearch Centre for Sustainable Process Technology, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia

^bFaculty of Science & Technology, Universiti Kebangsaan Malaysia

*Corresponding author: mashi_152@yahoo.com

Received 4 March 2018, Received in revised form 31 October 2018

Accepted 8 February 2019, Available online 30 April 2019

ABSTRACT

The depletion of petroleum sources and global warming issues has increased awareness among scientists to produce alternative energy other than the one that we always depend on, which is petroleum. Hydrogen (H_2) energy is one of the alternatives that was promising as an efficient and green fuel. Meanwhile, formic acid has been detected as one of the convenient H_2 source/storage material. Here, we introduce two heterogeneous catalysts for H_2 generation from formic acid. $Fe_{0.1}Zn_{0.9}$ and $Fe_{0.5}Zn_{0.5}$ were synthesized by a modified microwave method. In this study, we report the result of a detailed study undertaken to investigate the decomposition of formic acid to H_2 and carbon dioxide (CO_2) using gas chromatography with thermal conductivity detector (GC-TCD). The catalyst used to decompose the formic acid was characterized by x-ray diffraction (XRD) to determine their physicochemical properties. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were also used to determine the surface morphology and the structure of the synthesized catalysts. The result suggested that in the dehydrogenation reaction, 90-96% of H_2 was selectively produced from the formic acid with the presence of FeZn catalyst. For $Fe_{0.1}Zn_{0.9}$ catalyst, FESEM micrograph shows the particle was well dispersed, existing both away from and close proximity to 50-70 nm in size. Both heterogeneous catalysts are able to produce H_2 from formic acid at room temperatures ($30^\circ C$) with no additives added and with high selectivity.

Keywords: H_2 Energy; Fezn Catalyst; Formic Acid Decomposition; Microwave-assisted Method; H_2 Selectivity

ABSTRAK

Sumber petroleum yang semakin berkurang dan isu pemanasan global telah meningkatkan kesedaran di kalangan saintis untuk menghasilkan tenaga alternatif selain daripada sumber petroleum yang kita selalu gunakan. Tenaga hidrogen (H_2) adalah salah satu alternatif yang menjanjikan sebagai bahan api yang cekap dan hijau. Sementara itu, asid formik telah dikenal pasti sebagai salah satu sumber/penyimpan H_2 yang bagus. Di sini, kami memperkenalkan dua mangkin heterogen untuk penghasilan H_2 daripada asid formik. $Fe_{0.1}Zn_{0.9}$ dan $Fe_{0.5}Zn_{0.5}$ telah disintesis dengan menggunakan kaedah gelombang mikro yang diubah suai. Dalam kajian ini, kami melaporkan hasil kajian terperinci yang dilakukan untuk mengkaji penguraian asid formik kepada H_2 dan karbon dioksida (CO_2) menggunakan gas kromatografi dengan pengesan konduktiviti terma (GC-TCD). Mangkin yang digunakan untuk mengurai asid formik dicirikan oleh pembelauan sinar-X (XRD) untuk menentukan sifat fiziko-kimia mereka. Mikroskopi imbasan elektron dengan tenaga penyerakan (FESEM) dan mikroskopi elektron transmisi (TEM) juga digunakan untuk menentukan morfologi permukaan dan struktur mangkin yang disintesis. Hasilnya menunjukkan bahawa dalam tindak balas dehidrogenasi, asid formik dapat menghasilkan 90-96% H_2 secara selektif dengan kehadiran mangkin FeZn. Bagi mangkin $Fe_{0.1}Zn_{0.9}$, mikrograf FESEM menunjukkan bahawa zarah tersebut tersebar dengan baik, yang bersaiz 50-70 nm. Kedua-dua mangkin heterogen dapat menghasilkan H_2 daripada asid formik pada suhu bilik ($30^\circ C$) tanpa tambahan aditif dan dengan kepilihan yang tinggi.

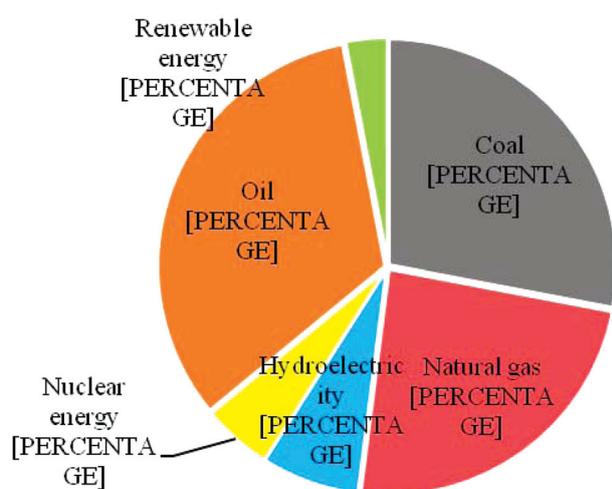
Kata kunci: Tenaga H_2 ; Mangkin Fezn; Penguraian Asid Formik; Kaedah Berbantu Gelombang Mikro; Kepilihan H_2

INTRODUCTION

According to a report from the United Nations, the world population reached 7.6 billion as of December 2017

indicating a growth of one billion in the last eleven years and expected to increase to 11.8 billion by the year 2100. The increment of the world's population has been coincided with a great technological development since the industrial

revolution and has resulted in an ever-increasing energy demand by humankind. Figure 1 shows the percentage of world energy consumption in the year 2016. The consumption of petroleum-based energy such as fossil fuel and coal were about 4418.2 mtoe (33%) and 3732.0 mtoe (28%), respectively. While the energy consumption from renewable sources was only 3% of the total consumption of world energy, which is 419.6 mtoe (BP Statistical Review 2017). The consumption of petroleum-based fuel in varieties of industry and the use of it as major source of energy in vehicles have led to the increase of toxic gases such as CO_2 , SO_2 , and NO_x due to the combustion of the fuel and the liberation of the produced gases to atmosphere hence causes global warming (El Naggat & Akay 2013; El Naggat et al. 2016; Marbán & Valdés-Solis 2007). Moreover, the fossil fuel consumed is not a sustainable source and will deplete anytime. So, the substitution of fossil fuel to a more sustainable energy source such as hydrogen gas (H_2) will solve the problem. H_2 is the future energy that can be produced by water splitting ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$), methane steam reforming ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$) (Yoo et al. 2015), decomposition of formic acid ($\text{CHOOH} \rightarrow \text{H}_2 + \text{CO}_2$) (Bi et al. 2016; Mandal et al. 2015; Montandon-Clerc et al. 2015) and others (Satar et al. 2016). Hydrogen is very dependable due to its clean combustion pathways and high gravimetric energy density as a future energy carrier (Montandon-Clerc et al. 2015).



Source: BP Statistical Review of World Energy, Jun 2016

FIGURE 1. Percentage of energy consumption of the year 2016

In this research, we decompose formic acid to generate H_2 because according to Celaje et al. (2016), formic acid is a promising energy carrier for the on-demand H_2 generation as it also is a form of stored H_2 because the reverse reaction of formic acid decomposition is also possible. Moreover, formic acid can also be prepared by synthesis from biomass (Jia et al. 2014), recycling carbon dioxide by catalytic hydrogenation (Bernskoetter & Hazari 2017; Weilhard et al. 2018) or

electrochemical reduction (Feaster et al. 2017). Formic acid can undergo two possible pathways, i.e. dehydrogenation and dehydration. The latter reaction should be avoided in order to complete this research work. This is due to the carbon monoxide (CO) gas that would be produced by dehydration pathway, which will be the poison to the catalyst used in the reaction. This could not happen as it may decrease the activity of catalyst (Tedsree et al. 2011; Wang et al. 2014). Below are the two pathways of formic acid decomposition in order to understand more.

	ΔG_{298K} (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	
$\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$	-35.0	31.2	215	(1)
$\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$	-14.9	28.7	138	(2)

Equation (1) shows the dehydrogenation reaction of a formic acid, while equation (2) is the dehydration reaction. The dehydrogenation reaction shows more negative value (-35.0 kJmol⁻¹) which indicate that the decomposition of formic acid to H_2 and CO_2 is thermodynamically more favorable than dehydration of formic acid. A vast number of studies have been performed over metal-based heterogeneous catalysts on the formic acid decomposition to H_2 , such as Pd (Jeon et al., 2016), Au (Bi et al. 2016), Ir (Celaje et al. 2016), Ag (Mandal et al. 2015) and Fe (Stathi et al. 2015). Flaherty et al. (2010) found that the type of catalyst used in the reaction affects the reaction whether it undergoes dehydration or dehydrogenation. Hence, in this study, we develop a catalyst that can generate H_2 for a future energy from formic acid.

METHODOLOGY

SYNTHESIS OF CATALYSTS

All chemicals were of analytical grades and were used without further purification. FeZn bimetallic catalysts were prepared by microwave combustion method with the weight percentage (wt%) of Fe to Zn as 10:90 and 50:50. For the synthesis of the catalyst, an appropriate amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with ratio stated before were mixed in a beaker and then ethylene glycol: water (0.75:0.25) solution was added as reducing agent. The mixture was then stirred with a magnetic stirrer at room temperature until all salts are soluble in the solution. The precipitate was obtained by adding 10M of KOH into the solution until the pH value of the mixed solution achieved 10 under vigorous stirring at room temperature. After that, the beaker was put into a microwave with a power of 800 W for 2 min. The product was separated by centrifugation (800 rpm, 10 min), washed with distilled water, ethanol and acetone several times, and dried in an oven at 115°C for 15 min. The product was then reduced in hydrogen gas at 550°C for 2 hours to get FeZn bimetallic.

CHARACTERIZATION OF CATALYST

X-ray diffraction (XRD) diffractogram of the produced catalysts was recorded on a Bruker AXS D8 Advance using a Cu K α radiation source (40 kV, 40 mA). Scans were taken over the 2 θ range from 10° to 80° and wavelength, $\lambda = 0.154$ nm. 1 gram of sample was put on a sample holder. The data obtained from the analysis were compared with standard peak data reported by the Joint Committee on Powder Diffraction Standard (JCPDS) to get the structure and identity of the sample. A Zeiss MERLIN field emission scanning electron microscopy (FESEM) was used for morphological studies. A Philip CM 12 transmission electron microscope (TEM) at 120 kV was used to investigate the microstructure of the synthesized FeZn catalysts. The FeZn catalyst was dispersed in acetone and then dropped on carbon-coated films and dried at room temperature for TEM study.

CATALYTIC DECOMPOSITION OF FORMIC ACID

Catalytic decomposition of formic acid over 0.15 g of FeZn bimetallic catalysts were performed at room temperature in a closed glass reactor containing 1 g of 50% formic acid in water. The gaseous products were collected using a gas bag which connected to the reactor and manually injected to GC-TCD every 30 min for 120 min. The selectivity of H₂ gas for every collected data was reported in the results section.

RESULTS & DISCUSSIONS

CRYSTALLINITY AND MORPHOLOGY

XRD diffractograms for fresh FeZn bimetallic catalysts are shown in Figure 2. The XRD pattern of all the samples has well-defined diffraction patterns with strong and sharp diffraction peaks, indicating that both are crystalline. The peaks at 31.74°, 34.42°, 36.24°, 47.47°, 56.56°, 62.80°, 66.41°, 67.89° and 69.02° are assigned to FeZnO (100), (002), (101), (102), (110), (103), (200), (112) and (201) respectively according to JCPDS 01-080-7102. There are no significant

peaks represented to single Fe metallic was detected for 10% Fe-Zn catalyst, but the Fe peaks were clearly observed in 50% Fe loading which shows at 44.72° and 65.01° that assigned to Fe (110) and (200) respectively according to JCPDS 01-087-0721. This suggests that new active Fe sites are available for the formic acid dehydrogenation reaction compare to Fe_{0.1}Zn_{0.9} catalyst. Noticeably, the increase of Fe concentration decreases the intensity of most of the peaks, indicating the degeneration of the crystalline quality. According to Mohd Ibrahim et al. (2015), it is believed that the Fe doping can reduce crystallinity. However, the presence of zinc is important too as Gao et al. (2016) state that the presence of Zn improves the catalyst stability in the reaction.

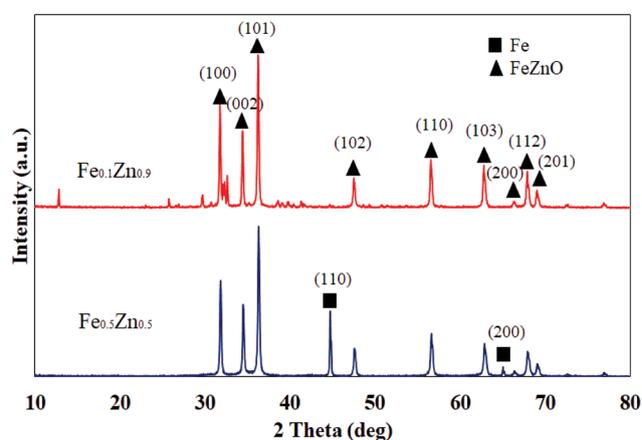


FIGURE 2. XRD diffractogram of Fe_{0.1}Zn_{0.9} and Fe_{0.5}Zn_{0.5}

Figure 3 shows the FESEM image of Fe_{0.1}Zn_{0.9} and Fe_{0.5}Zn_{0.5} at 50,000x magnification. The morphology of Fe_{0.5}Zn_{0.5} has better homogeneity in size and shape compared with Fe_{0.1}Zn_{0.9}. It may be due to the increasing of metallic particles and less ZnO formation on the surfaces during catalyst preparation. The presence of a little amount of ZnO can prevent the acid-base reaction between a formic acid (FA) and metal (Fe/Zn) which are not formed in a more stable alloy structure.

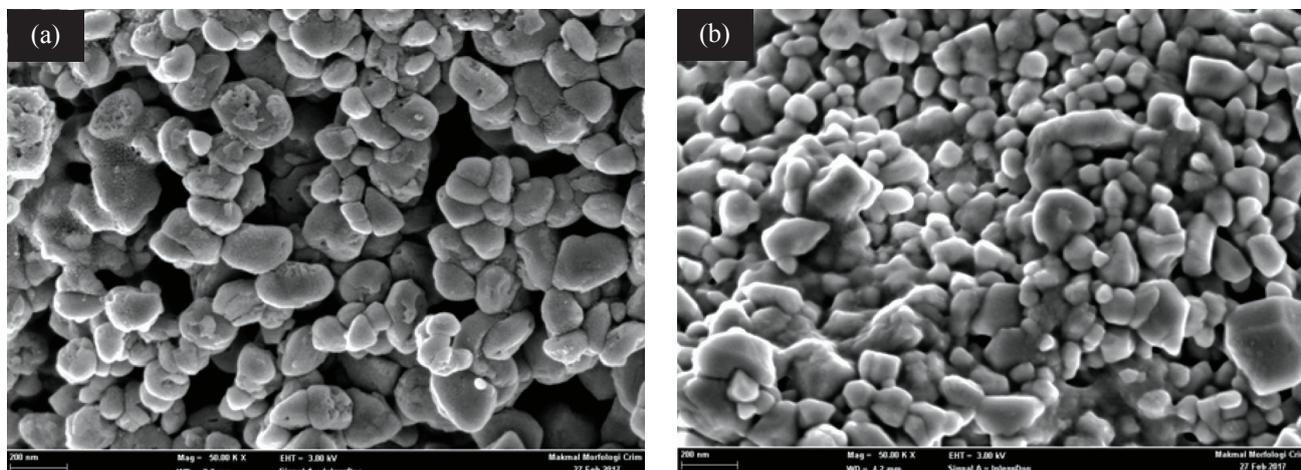


FIGURE 3. FESEM image of (a) Fe_{0.1}Zn_{0.9}; (b) Fe_{0.5}Zn_{0.5}

The TEM images of $\text{Fe}_{0.1}\text{Zn}_{0.9}$ and $\text{Fe}_{0.5}\text{Zn}_{0.5}$ nanoalloy at 35,000x magnification are as shown in Figure 4. The presence of a higher amount of Fe at ratio Fe: Zn of 1:1 has shown less agglomeration of particles ranging of 50 to 70 nm in

size. The presence of higher Fe content in Fe-Zn mixture can reduce the sintering effect and subsequently enhance the formation of active sites which offers higher potential in catalytic performance (Azizi et al. 2018).

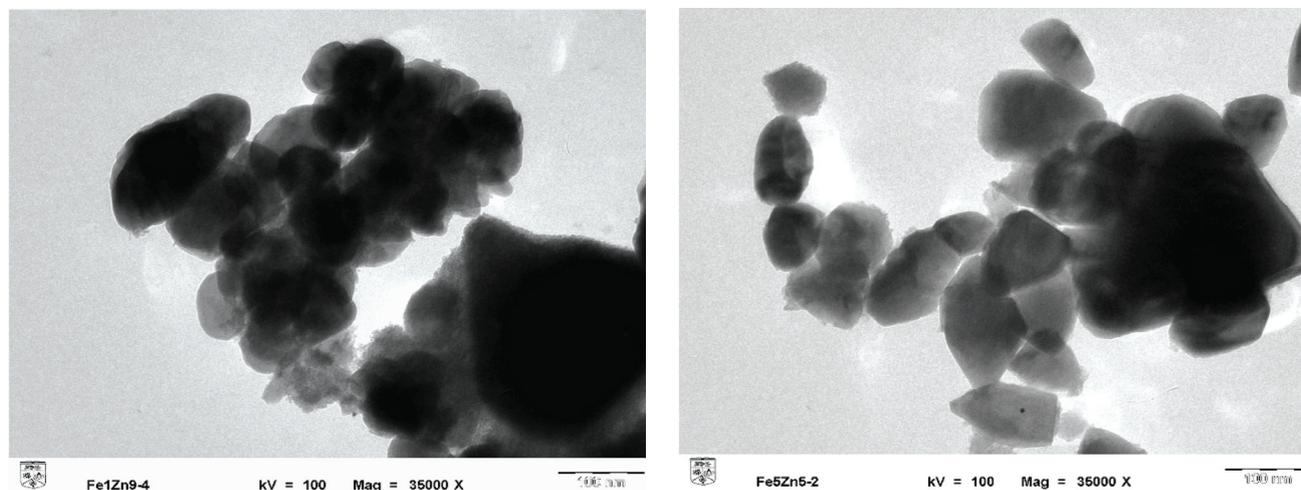


FIGURE 4. TEM image of (a) $\text{Fe}_{0.1}\text{Zn}_{0.9}$; (b) $\text{Fe}_{0.5}\text{Zn}_{0.5}$

CATALYTIC ACTIVITY OF THE FEZN CATALYSTS FOR FORMIC ACID DECOMPOSITION

It was said that PdAu catalysts are highly active for the dehydrogenation of formic acid, with almost complete selectivity, but at a higher temperature (92°C) (Huang et al. 2010; Zhou et al. 2008) than ours. In this research, FeZn catalyst can produce hydrogen at only room temperature. Moreover, Fe and Zn are non-precious metals, so they are less expensive than AuPd catalyst. In the presence of the FeZn bimetallic catalyst was showed a good reaction performance and selectivity of H_2 and CO_2 over FeZn catalysts at room temperature. The different metal ratio of the produced catalysts showed a significant effect on hydrogen selectivity over time.

Figure 5 shows the graph of H_2 production from 1 g 50% formic acid against time using two different catalysts with 0.15g each. As the time increases, the selectivity of H_2 by using $\text{Fe}_{0.1}\text{Zn}_{0.9}$ decreases whereas surprisingly increases for $\text{Fe}_{0.5}\text{Zn}_{0.5}$. This suggests the degradation of $\text{Fe}_{0.1}\text{Zn}_{0.9}$ activity over time while the opposite happens for $\text{Fe}_{0.5}\text{Zn}_{0.5}$. The degradation of the catalysts' activity is due to the decreases of formic acid concentration during the reaction process which some of them consumed and decompose into hydrogen and carbon dioxide (Wang et al. 2014). From this observation, it was found that both $\text{Fe}_{0.1}\text{Zn}_{0.9}$ and $\text{Fe}_{0.5}\text{Zn}_{0.5}$ catalysts have excellent H_2 selectivity. The selectivity for H_2 formation for $\text{Fe}_{0.1}\text{Zn}_{0.9}$ was 95.3-96.0% even though the activity of the catalyst decreases over time. As for $\text{Fe}_{0.5}\text{Zn}_{0.5}$ catalyst, the H_2 selectivity goes up from 90.0% to 94.3% in two hours reaction time. This may be due to the formation of Fe active sites that help to increase the selectivity. Furthermore, there is no CO formation from both of this reaction. This has been proved by a GC-TCD result that shows no peak for CO.

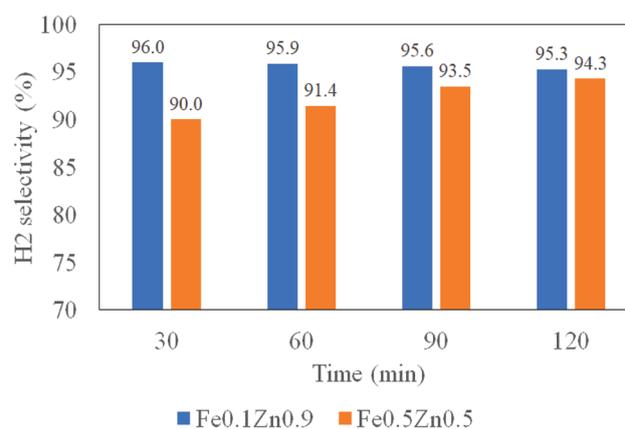


FIGURE 5. Production of H_2 from formic acid for 120 minutes

CONCLUSION

FeZn bimetallic nanocatalysts were successfully synthesized by co-precipitation assisted microwave method. The increment of Fe loading on the bimetallic catalyst shows the variable size of particles compares to lower Fe loading of 10%. The non-precious bimetallic catalysts were showed good performance on H_2 production via formic acid decomposition at low temperature. This work demonstrated that the addition of Zn modifies both the structure and activity of the catalysts, such that lowering the selectivity for CO_2 . The microwave method improves the dispersion of Fe and Zn phases resulting in better H_2 conversion and selectivity. Moreover, the complete conversion of formic acid to only H_2 and CO_2 make the catalysts work perfectly without the disturbance from other impurities such as CO that can degrade

the catalysts' activity. Moreover, the utilization of economic transition metals, which is Fe and Zn to produce such great catalyst for the dehydrogenation of formic acid may represent a new way to the development of an active and selective catalyst at room temperature.

ACKNOWLEDGMENT

The authors wish to thank Universiti Kebangsaan Malaysia (UKM) and the Ministry of Higher Education for funding this project under research grant, DIP-2016-010 and FRGS/1/2015/SG01/UKM/02/2, respectively. The authors also wish to thank the Centre of Research and Innovation Management (CRIM), UKM for the use of their instruments.

REFERENCES

- Azizi, M.A. H., Isahak, W.N.R.W., Masdar, M.S., Somalu, M.R. & Yarmo, M.A. 2018. Enhanced hydrogen selectivity from catalytic decomposition of formic acid over FeZnIr nanocatalyst at room temperature. *Research on Chemical Intermediates* 44(10): 1-16.
- Bernskoetter, W.H. & Hazari, N. 2017. Reversible hydrogenation of carbon dioxide to formic acid and methanol: lewis acid enhancement of base metal catalysts. *Accounts of Chemical Research* 50(4): 1049-1058.
- Bi, Q.Y., Lin, J.D., Liu, Y.M., He, H.Y., Huang, F.Q. & Cao, Y. 2016. Gold supported on zirconia polymorphs for hydrogen generation from formic acid in base-free aqueous medium. *Journal of Power Sources* 328: 463-471.
- Celaje, J.J.A., Lu, Z., Kedzie, E.A., Terrile, N.J., Lo, J.N. & Williams, T.J. 2016. A prolific catalyst for dehydrogenation of neat formic acid. *Nature Communications* 7: 11308-11313.
- El-Naggar, A.M.A. & Akay, G. 2013. Novel intensified catalytic nano-structured nickel-zirconia supported palladium based membrane for high temperature hydrogen production from biomass generated syngas. *International Journal of Hydrogen Energy* 38(16): 6618-6632.
- El-Naggar, A.M.A., Awadallah, A.E. & Aboul-Enein, A.A. 2016. Novel intensified nano-structured zero-valente nickel alloy based catalyst for hydrogen production via methane catalytic decomposition. *Renewable and Sustainable Energy Reviews* 53: 754-765.
- Feaster, J.T., Shi, C., Cave, E.R., Hatsukade, T., Abram, D.N., Kuhl, K.P., Hahn, C., Nørskov, J.K. & Jaramillo, T.F. 2017. Understanding selectivity for the electrochemical reduction of carbon dioxide to formic acid and carbon monoxide on metal electrodes. *ACS Catalysis* 7(7): 4822-4827.
- Flaherty, D.W., Berglund, S.P. & Mullins, C.B. 2010. Selective decomposition of formic acid on molybdenum carbide: a new reaction pathway. *Journal of Catalysis* 269(1): 33-43.
- Gao, P., Graham, U.M., Shafer, W.D., Liganiso, L.Z., Jacobs, G. & Davis, B.H. 2016. Nanostructure and kinetic isotope effect of alkali-doped Pt/silica catalysts for water-gas shift and steam-assisted formic acid decomposition. *Catalysis Today* 272: 42-48.
- Huang, Y., Zhou, X., Yin, M., Liu, C. & Xing, W. 2010. Novel PdAu @ Au/C core - shell catalyst: superior activity and selectivity in formic acid decomposition for hydrogen generation. *Chemistry of Materials* 22(6): 5122-5128.
- Jeon, M., Han, D.J., Lee, K.S., Choi, S.H., Han, J., Nam, S.W. & Jang, S.C. 2016. Electronically modified Pd catalysts supported on N-doped carbon for the dehydrogenation of formic acid. *International Journal of Hydrogen Energy* 41(34): 15453-15461.
- Jia, L., Bulushev, D.A. & Ross, J.R.H. 2014. Formic acid decomposition over palladium based catalysts doped by potassium carbonate. *Catalysis Today* 259: 453-459.
- Mandal, K., Bhattacharjee, D. & Dasgupta, S. 2015. Synthesis of nanoporous PdAg nanoalloy for hydrogen generation from formic acid at room temperature. *International Journal of Hydrogen Energy* 40(14): 4786-4793.
- Marbán, G. & Valdés-Solís, T. 2007. Towards the hydrogen economy? *International Journal of Hydrogen Energy* 32(12): 1625-1637.
- Mohd, I.R., Markom, M. & Abd, R.K.F. 2015. Optical properties of Fe²⁺ ion doped ZnS nanoparticles synthesized using co-precipitation method. *Jurnal Kejuruteraan* 27(1): 87-94.
- Montandon-Clerc, M., Dalebrook, A.F. & Laurency, G. 2015. Quantitative aqueous phase formic acid dehydrogenation using iron(II) based catalysts. *Journal of Catalysis* 343: 62-67.
- Satar, I., Ghasemi, M., Aljlil, S.A., Wan, I.W., Abdalla, A.M. & Alam, J. 2016. Production of hydrogen by *Enterobacter aerogenes* in an immobilized cell reactor. *International Journal of Hydrogen Energy* 42(14): 9024-9030.
- Stathi, P., Deligiannakis, Y., Avgouropoulos, G. & Loulodi, M. 2015. Efficient H₂ production from formic acid by a supported iron catalyst on silica. *Applied Catalysis A: General* 498: 176-184.
- Tedsree, K., Li, T., Jones, S., Chan, C.W.A., Yu, K.M.K., Bagot, P.A.J., Marquis, E.A., Smith, G.D.W. & Tsang, S.C.E. 2011. Hydrogen production from formic acid decomposition at room temperature using a Ag-Pd core-shell nanocatalyst. *Nature Nanotechnology* 6(5): 302-307.
- United Nations, Department of Economic and Social Affairs, Population Division, World Population Prospects, The 2017 Revision, Key Findings and Advance Tables. Working Paper. <https://esa.un.org/unpd/wpp/Download/Standard/Population/> [7 February 2017].
- Wang, Z.L., Ping, Y., Yan, J.M., Wang, H.L. & Jiang, Q. 2014. Hydrogen generation from formic acid decomposition at room temperature using a NiAuPd alloy nanocatalyst.

- International Journal of Hydrogen Energy* 39(10): 4850-4856.
- Weilhard, A., Qadir, M.I., Sans, V. & Dupont, J. 2018. Selective CO₂ hydrogenation to formic acid with multifunctional ionic liquids selective CO₂ hydrogenation to formic acid with multifunctional ionic liquids. *ACS Catalysis* 8(3): 1628-1634.
- Yoo, J., Bang, Y., Han, S.J., Park, S., Song, J.H. & Song, I.K. 2015. Hydrogen production by tri-reforming of methane over nickel-alumina aerogel catalyst. *Journal of Molecular Catalysis A: Chemical* 410: 74-80.
- Zhou, X., Huang, Y., Xing, W., Liu, C., Liao, J. & Lu, T. 2008. High-quality hydrogen from the catalyzed decomposition of formic acid by Pd-Au/C and Pd-Ag/C. *Chemical Communications* (30): 3540-3542.

*Masitah Abdul Halim Azizi,
Wan Nor Roslam Wan Isahak
Research Centre for Sustainable Process Technology,
Faculty of Engineering & Built Environment,
Universiti Kebangsaan Malaysia, Malaysia.

Norliza Dzakaria, Mohd Ambar Yarmo
School of Chemistry Science & Food Technology,
Faculty of Science & Technology,
Universiti Kebangsaan Malaysia, Malaysia