

Towards Autothermal Hydrogen Production by Sorption Enhanced Methanol to Shift: A Novel Concept

D. Iruretagoyena^{1,2*}, K. Hellgardt¹, N. Mac Dowell², D. Chadwick¹, N. Shah^{1,2}

¹ Department of Chemical Engineering; ² Centre for Process Systems Eng., Imperial College London, SW7 2AZ, UK

*Corresponding author: d.iruretagoyena09@imperial.ac.uk

Highlights

- The H₂ productivity and energy efficiency of the WGS is significantly enhanced by the addition of methanol and removal of CO₂ in situ (SEMETS)
- Commercial Cu-Zn and novel in-house synthesized Pt/CeO₂ catalysts display excellent catalytic performance for SEMETS, in the presence of hydrotalcite-based CO₂ adsorbents
- A dynamic model is developed and validated for the simulation of a cyclically operated SEMETS reactor

1. Introduction

Hydrogen (H₂) is one of the most important raw materials for the chemical and refinery industries worldwide. In addition, the use of H₂ as an ultraclean fuel in the transport and heat sectors has the potential to provide deep carbon emission reductions [1]. This has placed an imperative on improving the efficiency of steam reforming of hydrocarbons (SRH), this process being considered the most feasible and economic route to large scale H₂ production. A typical SRH plant includes a reformer followed by a water gas shift (WGS) stage and purification section. The energy efficiency of the reformer has increased significantly in recent years but there has been little progress on the improvement of the efficiency of the shift reactors. Among the few attempts to enhance the performance of the WGS section is the methanol-to-shift (MTS) process developed by Haldor Topsøe [2], which combines the exothermic WGS and the endothermic methanol reforming aiming to minimise the energy losses while boosting the H₂ productivity (up to 25%). The efficiency of the WGS can also be enhanced if it is combined with the in situ removal of CO₂ using a solid adsorbent. This shifts the equilibrium towards the products thereby increasing the production of H₂ [3].

Recently, we have reported a detailed thermodynamic analysis of the WGS and methanol steam reforming with simultaneous CO₂ adsorption (sorption enhanced methanol-to-shift, SEMETS) under typical operating conditions for SRH [4]. The results show that adding methanol to the feed enhances significantly the amount of H₂ produced and allows for autothermal operation of the shift unit. Further H₂ enhancement is achieved by separating CO₂ in situ. In this contribution, we present the first comprehensive experimental study of SEMETS. The effects of temperature, pressure, steam, methanol addition, fraction of CO₂ removed, and energy efficiency of the shift system are investigated. The performance of different commercial shift catalysts and a series of novel in-house synthesised catalysts are assessed in the presence of hydrotalcite-based adsorbents (HTs). A dynamic model is developed and validated for the simulation of a cyclically operated SEMETS reactor.

2. Methods

Commercial mid/high temperature shift catalysts (Cu/ZnO, Fe/Cr, CoMo) and a series of novel in-house synthesized catalysts (Pt/Al₂O₃, Pt/SiO₂, Pt/CeO₂/SBA15, Pt/CeO₂/ZrO₂ and Pt/CeO₂) were tested under optimal operating conditions for SEMETS [4]. In addition, hydrotalcite based adsorbents (including novel carbon and silica supported HTs) were prepared via a co-precipitation technique (see details in [5]). Transient and steady state catalytic and adsorption experiments were carried out in a stainless steel fixed bed reactor and the product evolution was measured by online mass spectrometry. The gases were fed using mass flow controllers, and steam and methanol vapors were supplied by an electrically heated vaporisation system. Breakthrough curve responses were obtained using an automated 4-way valve. After the catalysts were activated (573 K, 10% H₂/N₂), they were screened by conducting the reverse WGS and methanol decomposition under a temperature program. Stability tests of SEMETS were carried out at 573 K and 673 K for more than 24h. The enhancement of the MTS by CO₂ adsorption was evaluated by comparing the transient H₂ production in the presence and absence of adsorbent. The catalysts and CO₂ adsorbents were characterised by a range of physicochemical techniques (e.g. BET, TGA, XRD, TEM, ICP and TPR). A one

dimensional dynamic reactor model was developed to describe the performance of the SEMTS experimental results. The model was solved using gPROMS.

3. Results and discussion

The CO, CH₄ and CO₂ yields obtained at 573 K and 673 K during the TPR-methanol decomposition over the different catalysts tested are presented in Table 1. The mid-temperature Cu-Zn catalyst shows high conversions of methanol to CO and H₂ between 573 and 773 K with a negligible methane production. The amount of CO₂ produced is likely to be associated to the Boudouard reaction and α -brass alloy formation. The high temperature Fe-Cr catalyst is less active than Cu-Zn, and produces significant CO₂ and methane at high temperature. Pt/Al₂O₃ and Pt/SiO₂ are inactive at 573 K but high conversions and remarkable selectivities to CO are observed between 673 and 773 K. The negligible formation of CO₂ is related to the non-reducibility of the supports under the conditions tested. In the presence of cerium oxide the activity of Pt at low temperatures is enhanced significantly while CO₂ formation increases very modestly. Co-Mo is found to be active under methanol decomposition but relatively high amounts of methane and CO₂ are detected. MoS₂ is known to catalyze the synthesis of methanol producing methane unless it is promoted with alkali metals. Analogous TPR-RWGS studies were carried out for all the catalysts (data not shown).

From the screening tests, Cu-Zn and Pt/CeO₂ are identified as the most promising candidates to catalyze the combined methanol reforming and water gas shift (i.e. MTS). Stability tests show that the activity and selectivity of both catalysts remain constant through WGS and MTS tests alone and with simultaneous CO₂ adsorption (in the presence of a HT adsorbent). It is worth mentioning that the water co-fed during MTS mitigates the deactivation of the Cu-Zn catalyst caused by carbon deposition. The transient experimental profiles (Figure 1) can be described using a dynamic sorption-enhanced reactor model. Literature rate equations for the WGS and methanol reforming reactions, and a linear driving force model can be used to describe the reaction and adsorption kinetics respectively.

Table 1. CO, CH₄ and CO₂ yields (%)
Conditions: PCH₃OH = 50 mbar, GHSV = 83060 hr⁻¹, 1 bar

Catalysts	573 K			673 K		
	YCO	YCH ₄	YCO ₂	YCO	YCH ₄	YCO ₂
Cu-Zn	0.50	0.01	0.14	0.73	0.03	0.17
Fe-Cr	0.05	0.01	0.06	0.33	0.22	0.42
Co-Mo	0.52	0.08	0.03	0.56	0.19	0.11
1% Pt/Al ₂ O ₃	0.03	0.00	0.00	0.46	0.01	0.00
1% Pt/SiO ₂	0.14	0.01	0.00	0.89	0.01	0.01
1% Pt/CeO ₂	0.55	0.01	0.03	0.77	0.05	0.15
1% Pt/20%CeO ₂ /SBA15	0.72	0.00	0.03	0.78	0.06	0.15
1%Pt/CeO ₂ /ZrO ₂	0.60	0.01	0.05	0.61	0.13	0.25

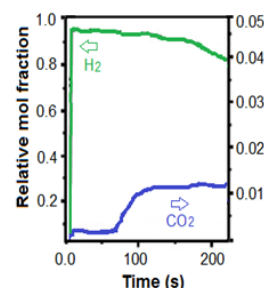


Figure 1. SEMTS over Cu-Zn and HT (1st cycle)

4. Conclusions

SEMTS appears as a promising technology to enhance the efficiency of the shift section while a CO₂ rich stream for sequestration is produced. The findings of this study suggest that among different commercial and in-house synthesized catalysts, Cu-Zn and novel Pt containing CeO₂ are promising candidates for SEMTS. The catalysts exhibit high activities and selectivities, and are stable under the relevant operating conditions (473 to 723 K) for MTS, in the presence and absence of hydrotalcite-based CO₂ adsorbents.

References

- [1] Committee on Climate Change, Next steps for UK heat policy, (2016) (<https://www.theccc.org.uk/wp-content/uploads/2016/10/Next-steps-for-UK-heat-policy-Committee-on-Climate-Change-October-2016.pdf>).
- [2] P. Nielsen, et al. US 7,527,781 B2 (2009)
- [3] H. M. Jang, et al., Chem. Eng. Sci., 73 (2012) 431-438
- [4] D. Iruretagoyena, et al. Int. J. Hydrog. Energy, under review (to be published by January 2018)
- [5] D. Iruretagoyena, Springer (2016), Switzerland.

Acknowledgements

This work is supported by the ELEGANCY, EU H2020 project and the EPSRC (UK) grant EP/N010531/1

Keywords

Hydrogen, water-gas-shift reaction, methanol reforming, sorption-enhancement, CO₂ adsorption

Diana Iruretagoyena

Address: 109 Gloucester Terrace, London W2 3HB, UK
Tel: +44 (0) 7397557599;
E-mail: d.iruretagoyena09@imperial.ac.uk



Brief CV

Dr. Diana Iruretagoyena obtained her PhD in the Department of Chemical Engineering (2014) at Imperial College London where she currently works as Research Associate. Her research focuses on the interfaces of reaction engineering, applied catalysis, separation processes and materials science combining laboratory experiments and modelling work. Overall the research deals with the study and development of new processes which aim to be economical, environmentally friendly and energy efficient. An important part of her work involves synthesis, characterization and testing of a wide range of nanostructured materials including carbon nanotubes and graphene composites, inorganic (hydro) oxides (e.g. hydrotalcites) and supported metal catalysts. The aim is to understand and tune the chemical properties and morphology of these materials so they can be successfully applied in various areas such as adsorption of CO₂ and organosulfur compounds, hydrogen production by process intensification (e.g. sorption enhanced water gas shift reaction) and catalytic production of chemical intermediates from bio-based feedstocks.

Diana's research has resulted in relevant scientific publications and has been presented in many prestigious international conferences and seminars. She is frequently invited to present her work at international forums, form part of scientific committees, join editorial boards and be reviewer in leading engineering journals. In addition, she has received several awards including the Prize for the best poster at ISCRE 22, the Julia Higgins Centenary Prize 2014 from the Department of Chemical Engineering, Imperial College London and the Springer Theses Award 2016 from Springer.

Education

- 2015-present **Research Associate**
Imperial College London (UK), Department of Chemical Engineering,
- Enabling a Low-Carbon Economy via Hydrogen and CCS (H2020, European project)
Supervisor: Prof. Nilay Shah (Head of Department)
 - Catalytic routes to intermediate sustainable process (EPSRC, UK)
Supervisor: Prof. David Chadwick
- 2010-2014 **PhD in Chemical Engineering (Julia Higgins Centenary Prize)**
Imperial College London, UK, Department of Chemical Engineering.
Supervisors: Prof. David Chadwick and Prof. Klaus Hellgardt
Thesis: Supported Layered Double Hydroxides as CO₂ Adsorbents for Sorption-enhanced H₂ Production
- 2007-2009 **M.Sc in Chemical Engineering, (1st class honours)**
Universidad Nacional Autónoma de México (UNAM), Department of Chemical Eng.
- Catalytic dimerization of pentenes using fluorinated alumina
- 2002-2006 **B.Sc in Chemical Engineering, (Best student among 200, Gabino Barreda Medal)**
Universidad Nacional Autónoma de México (UNAM), Department of Chemical Eng.
- Thermodynamic modelling of crude oil and gas blends from Mexican reservoirs"

Awards, Scholarships, Fellowships

- 2016 **Springer Theses Award** (Recognizing Outstanding Ph.D. Research, *the "best of the best"*), this series publishes annually the best theses of top-ranked institutes, each thesis is selected for its scientific excellence and impact on research.
(<http://www.springer.com/gb/book/9783319412757>)

2015	Associate Fellow of the Higher Education Academy (UK Professional Standards Framework)
2015	Julia Higgins Centenary Prize (Imperial College London): PhD thesis of exceptional merit in the broad areas of polymer science and materials engineering
2012	Prize for best poster at the 22nd International Symposium on Chemical Reaction Engineering (ISCRE 22) . Work presented: Supported Hydrotalcites for Sorption Enhanced Water Gas Shift Reaction
2007-2014	Scholarships awarded by CONACyT, SEP (Mexico) and ICL (UK) to study MEng. and PhD
2008	Gabino Barreda Medal in Chemical Engineering (B.Sc.): Highest award given by UNAM to the best student of each class of every bachelor

Publications

Books

1. Book chapter: [D. Iruretagoyena*](#), R. Montesano, Selective sulphur removal from liquid fuels using nanostructured adsorbents, In Principles and applications of nanotechnology in oil and gas industries. invited Chapter, Springer (2017), in press
2. Book: [D. Iruretagoyena*](#), [Supported Layered Double Hydroxides as CO₂ Adsorbents for Sorption-Enhanced H₂ Production](#), [Springer Theses \(2016\)](#), [Switzerland](#), <http://www.springer.com/gb/book/9783319412757>

Journal contributions

1. [D. Iruretagoyena](#), K. Hellgardt, D. Chadwick*, Towards autothermal hydrogen production by sorption-enhanced methanol reforming: A thermodynamic analysis, Int. J. Hydrogen Energy, under review, (to be published by January 2018).
2. J. Peng[‡], [D. Iruretagoyena[‡]](#), D. Chadwick*, Hydrotalcite/SBA15 composites for pre-combustion CO₂ capture: CO₂ adsorption characteristics. Journal of CO₂ Utilization. ([‡]These authors contributed equally to the work), accepted.
3. I. Graca, [D. Iruretagoyena[‡]](#), D. Chadwick*, Glucose Isomerisation into fructose over magnesium-impregnated NaY zeolite catalysts, Applied Catalysis B: Environmental (2017), ([‡]TPD measurements), DOI: 10.1016/j.apcatb.2017.01.037
4. R. Menzel[‡],*, [D. Iruretagoyena[‡]](#),*, Y. Wang, S. M. Bawaked, M. Mokhtar, S. A. Al-Thabaiti, S. N. Basahel, M. S. P. Shaffer, Graphene Oxide/Mixed Metal Oxide Hybrid Materials for Enhanced Dibenzothiophene Adsorption from Liquid Hydrocarbon Fuels, Fuel 181 (2016), 531-536. ([‡]These authors contributed equally to the work), DOI: 10.1016/j.fuel.2016.04.125
5. [D. Iruretagoyena](#), M. Shaffer and D. Chadwick*, Influence of alkali metals on GO supported LDHs for CO₂ adsorption, Ind. Eng. Chem. Res. 54 (2015), 11610-11618. DOI: 10.1021/acs.iecr.5b02762
6. [D. Iruretagoyena](#), M. Shaffer and D. Chadwick*, Layered Double Oxides Supported on Graphene Oxide for CO₂ Adsorption: Effect of support and residual sodium, Ind. Eng. Chem. Res. 54 (2015), 6781-6792. DOI:10.1021/acs.iecr.5b01215
7. Sanfiz, N. Morales, M. De Marco, [D. Iruretagoyena[‡]](#), M. Mokhtar, A. M. Asiri, S. N. Basahel, S. A. Al-Thabaiti, A. O. Alyoubi and M. S. P. Shaffer*, Self-condensation of acetone over Mg-Al layered double hydroxide supported on multi-walled carbon nanotube catalysts, J. Mol. Catal., 398 (2015) 50-57. ([‡]TPD measurements), DOI:10.1016/j.molcata.2014.11.002
8. [D. Iruretagoyena](#), M. Shaffer and D. Chadwick*, Adsorption of carbon dioxide on graphene oxide supported layered double oxides, Adsorption. 20 (2014) 321. DOI: 10.1007/s10450-013-9595-3
9. Garcia-Gallastegui[‡],*, [D. Iruretagoyena[‡]](#), V. Gouvea, M. Mokhtar, A. M. Asiri, S. N. Basahel, S. A. Al-Thabaiti, A. O. Alyoubi, D. Chadwick and M. S. P. Shaffer*, Graphene oxide as support for layered double hydroxides: Enhancing the CO₂ sorption capacity, Chem. Mater. 24 (2012) 4531. ([‡]These authors contributed equally to the work), DOI: 10.1021/cm3018264
10. Garcia-Gallastegui[‡],*, [D. Iruretagoyena[‡]](#), M. Mokhtar, A. M. Asiri, S. N. Basahel, S. A. Al-Thabaiti, A. O. Alyoubi, D. Chadwick and M. S. P. Shaffer*, Layered double hydroxides supported on multi-walled carbon nanotubes: preparation and CO₂ adsorption characteristics, J. Mater. Chem. 22 (2012) 13932. **Front Cover of the Journal**. ([‡]These authors contributed equally to the work), DOI: 10.1039/C2JM00059H

Conferences

Oral Presentations

1. [D. Iruretagoyena[‡]](#), M. Shaffer, D. Chadwick, Carbon supported hydrotalcites as CO₂ and sulphur adsorbents, 3rd International Conference on Energy Materials and Environment Engineering, Bangkok, Thailand, 2017 ([‡]speaker), **conference grant award, invited talk**
2. [D. Iruretagoyena[‡]](#), K. Hellgardt, D. Chadwick, Clean H₂ production by sorption enhancement using layered double hydroxides, 12th International Conference on the Fundamentals of Adsorption, Friedrichshafen, Germany, 2016 ([‡]speaker)
3. [D. Iruretagoyena[‡]](#), A. Garcia-Gallastegui, K. Hellgardt, M. Shaffer, D. Shaffer, D. Chadwick, Carbon supported layered double hydroxides for pre-combustion CO₂-capture. 3rd International Symposium on Energy Challenges and Mechanics-towards a big picture, Aberdeen, Scotland, UK, 2015. (speaker), **invited talk**

4. [D. Iruretagoyena](#)[‡], X. Huang, M. Shaffer, K. Hellgard and D. Chadwick, Graphene oxide supported hydrotalcites for pre-combustion CO₂ capture, 23rd International Symposium on Chemical Reaction Engineering, Bangkok, Thailand, 2014. ([‡]speaker)
5. [D. Iruretagoyena](#)[‡], M. Shaffer, D. Chadwick, Clean hydrogen production by process intensification, 3rd International Symposium on Green Chemistry, La Rochelle, France, 2015. ([‡]speaker)
6. [D. Iruretagoyena](#)[‡], M. Shaffer, D. Chadwick, Graphene oxide supported hydrotalcites for pre-combustion CO₂ capture, 23rd International Symposium on Chemical Reaction Engineering, Bangkok, Thailand, 2014 ([‡]speaker)
7. [D. Iruretagoyena](#)[‡], K. Hellgardt and D. Chadwick, Sorption enhanced water gas shift. Adsorption of CO₂ on carbon supported hydrotalcites, DICP, Dalian, China, 2014 (speaker), **invited talk**
8. [D. Iruretagoyena](#)[‡], A. Garcia-Gallastegui, K. Hellgardt, M. Shaffer and D. Chadwick, Adsorption of carbon dioxide on graphene oxide supported hydrotalcites, 11th International Conference on the Fundamentals of Adsorption, Baltimore, MD, USA, 2013. (speaker), **travel grant award, plenary session**
9. [D. Iruretagoyena](#)[‡], R. Montesano and M. Hernandez, Dimerization of isomaylene using fluorinated alumina as catalyst, Campus of Excellence, Gran Canaria, Spain, 2008. (speaker), **travel grant award**

Poster Presentations

10. R. Menzel, [D. Iruretagoyena](#)[‡], Y. Wang, Salem M. Bawaked, M. Mokhtar[‡], S. A. Al-Thabaiti, S. N. Basahel, M. S.P. Shaffer, Graphene Oxide/Mixed Metal Oxide Hybrid Materials for Enhanced Dibenzothiophene Adsorption from Liquid Hydrocarbon Fuels, 12th International Conference on the Fundamentals of Adsorption, Friedrichshafen, Germany, 2016. ([‡] speaker)
11. N. Morales[‡], [D. Iruretagoyena](#), D. Chadwick, Layered Double Hydroxide (LDH)/Carbon nanostructures (CNS) composites: activity study on condensation reactions, Catalysis, fundamentals and practice, Liverpool, U.K., 2016. ([‡] speaker)
12. N. Morales[‡], N. Pillai, T. Salim, [D. Iruretagoyena](#)[‡], D. Chadwick, Layered double hydroxides: activity analysis on condensation reactions, Applied Catalysis and Reaction Engineering IChemE, Cambridge, UK, 2014. ([‡] speaker)
13. [D. Iruretagoyena](#)[‡], A. Garcia-Gallastegui, K. Hellgardt, M. Shaffer and D. Chadwick, Supported hydrotalcites for sorption enhanced water gas shift reaction, 22nd International Symposium on Chemical Reaction Engineering, Maastricht, Netherlands, 2012. ([‡] speaker), **prize for best poster**
14. Garcia-Gallastegui[‡], [D. Iruretagoyena](#), M. Mokhtar, A. M. Asiri, S. N. Basahel, S. A. Al-Thabaiti, A. O. Alyoubi, D. Chadwick and M. S. P. Shaffer, Graphene oxide/Carbon nanotube supported layered double hydroxides for CO₂ capture applications, ChemOnTubes, France, 2012. ([‡] speaker)
15. Garcia-Gallastegui[‡], [D. Iruretagoyena](#), M. Mokhtar, A. M. Asiri, S. N. Basahel, S. A. Al-Thabaiti, A. O. Alyoubi, D. Chadwick and M. S. P. Shaffer, Graphene oxide supported layered double hydroxides for CO₂ capture applications, Graphene, Brussels, 2012. ([‡] speaker)