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CHEMICAL SCIENCES ROUNDTABLE

THE UNIVERSITY OF TOLEDO 1872

Dual-Function Materials for CO_2 Capture and Conversion

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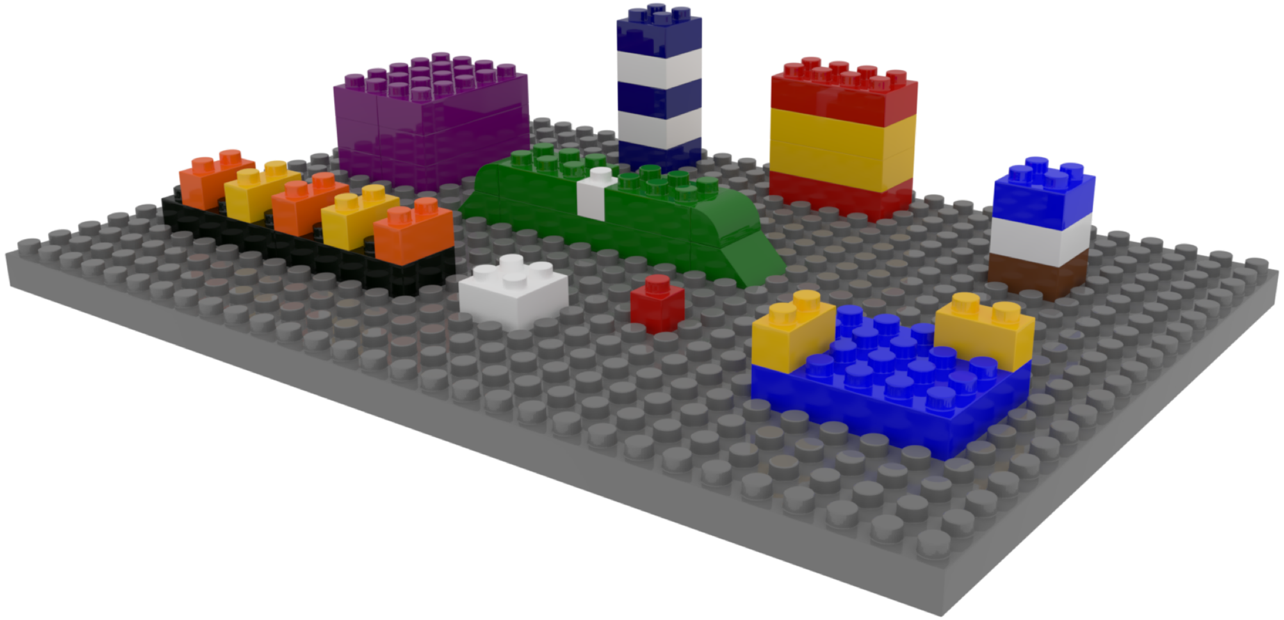
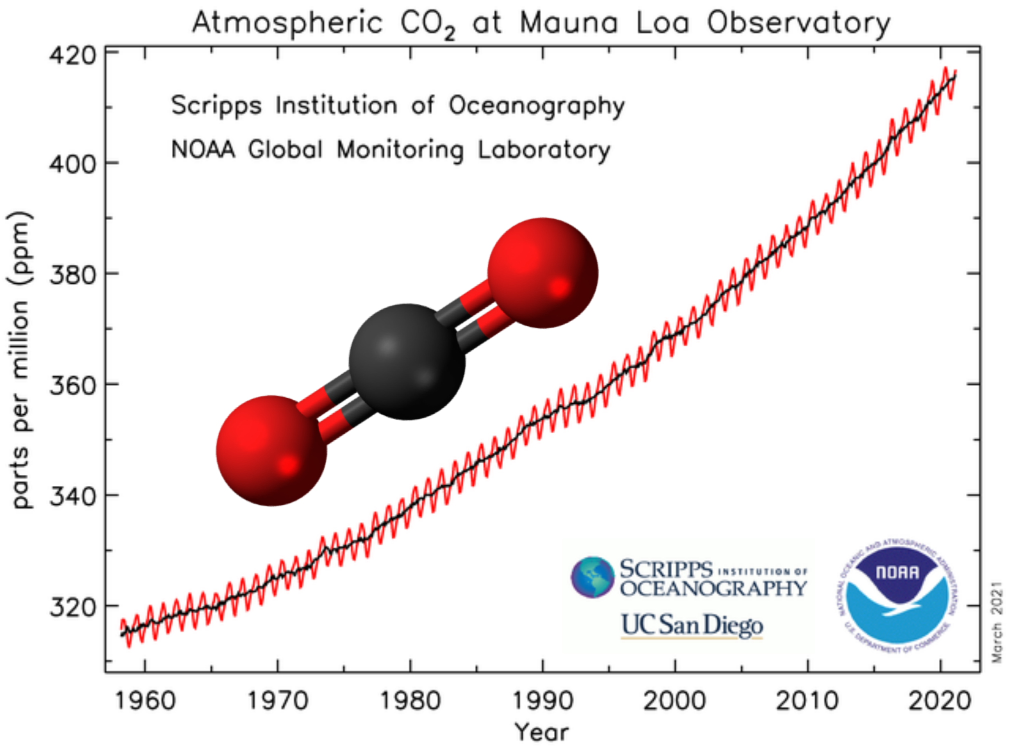
Alba-Rubio Group

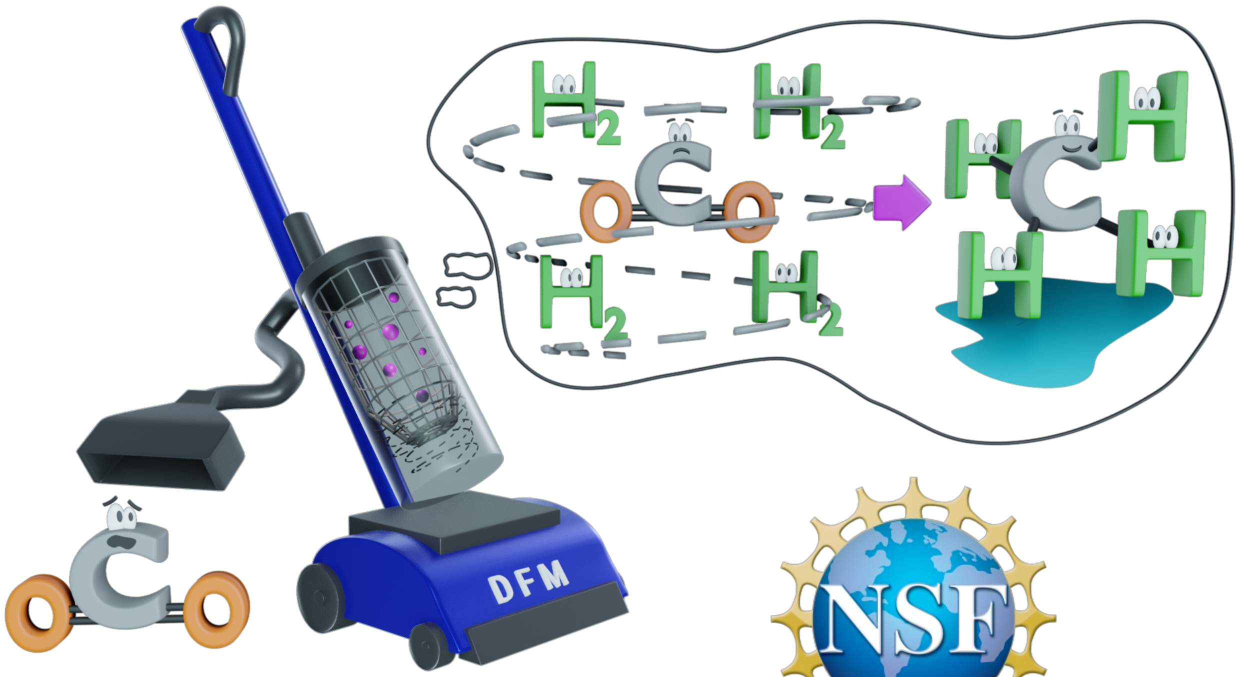
Our research focuses on the rational design and synthesis of nanomaterials for catalysis and sensing applications.

Multifunctional catalysts: Catalysts that perform different tasks during the course of a reaction.



Dual-Function Materials for CO_2 Capture and Conversion

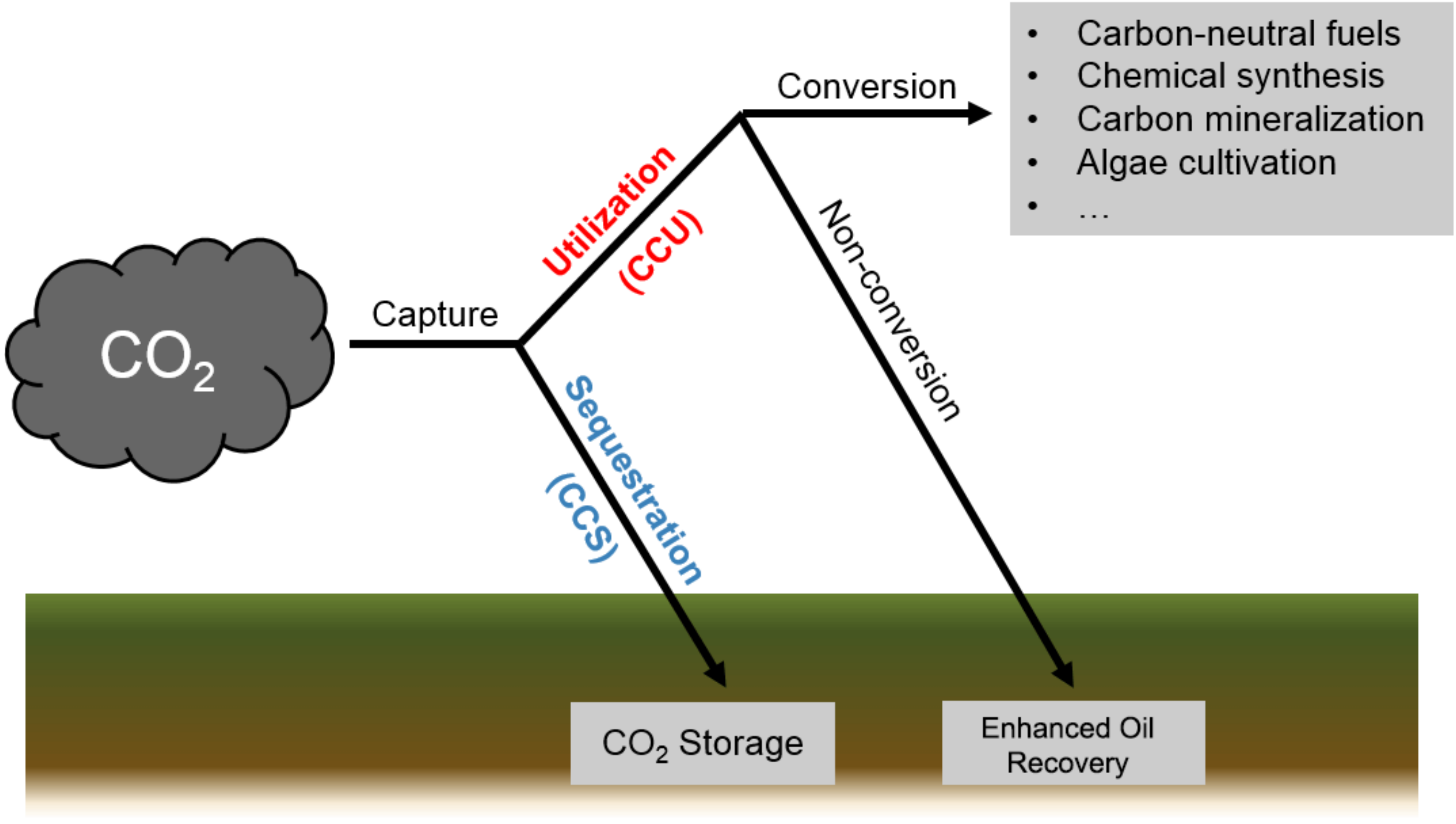




CAREER Award
3/1/2019-2/29/2024

https://www.esrl.noaa.gov/gmd/ccgg/trends/
I.S. Omodolor, H.O. Otor, J.A. Andonegui, B.J. Allen, A.C. Alba-Rubio; *Ind. Eng. Chem. Res.* 59 (40) **(2020)** 17612-17631.

Carbon Capture and Utilization (CCU) *vs* CCS



CCS

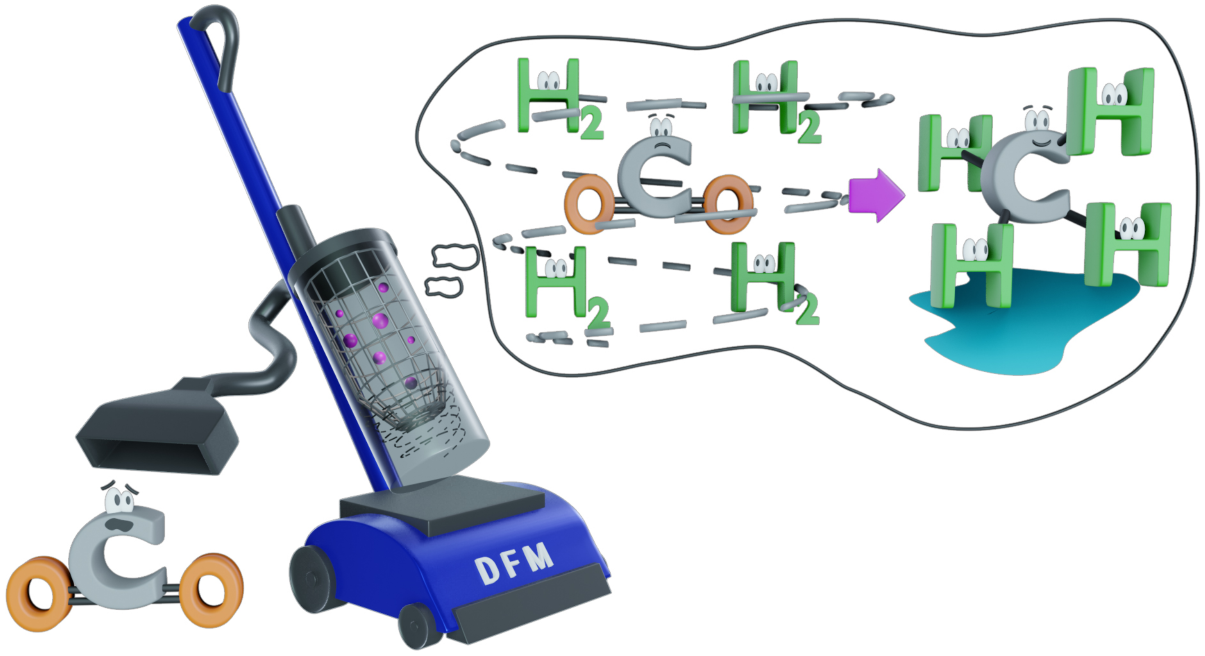
\+ CO_2 is concentrated, liquefied, and stored to minimize the emissions.

\+ Potential to reduce the CO_2 emissions from a power plant by 80-90%.

\- Thermal swing for CO_2 capture and regeneration of the sorbent.

\- Transportation and storage in geological formations.

Dual-Function Materials for CO_2 Capture and Conversion

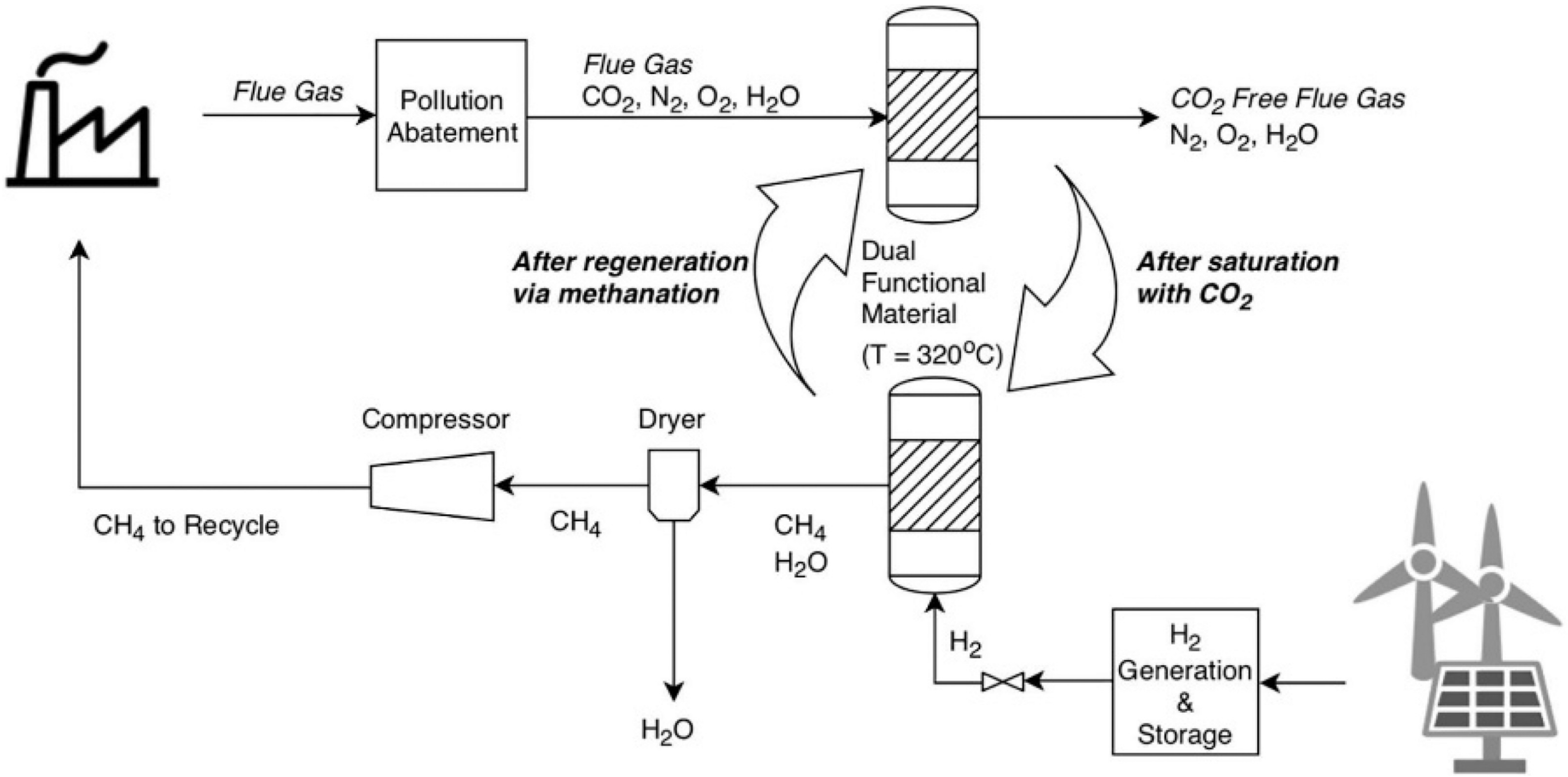


Advantages of DFMs

+ Both adsorbent and catalytic sites.
+ Can operate isothermally, eliminating thermal swing regeneration processes.
+ Can efficiently concentrate CO_2 from very diluted streams.
+ Eliminate transportation and storage.

I.S. Omodolor, H.O. Otor, J.A. Andonegui, B.J. Allen, A.C. Alba-Rubio; *Ind. Eng. Chem. Res.* 59 (40) **(2020)** 17612-17631.

Dual-Function Materials Process Flow Diagram



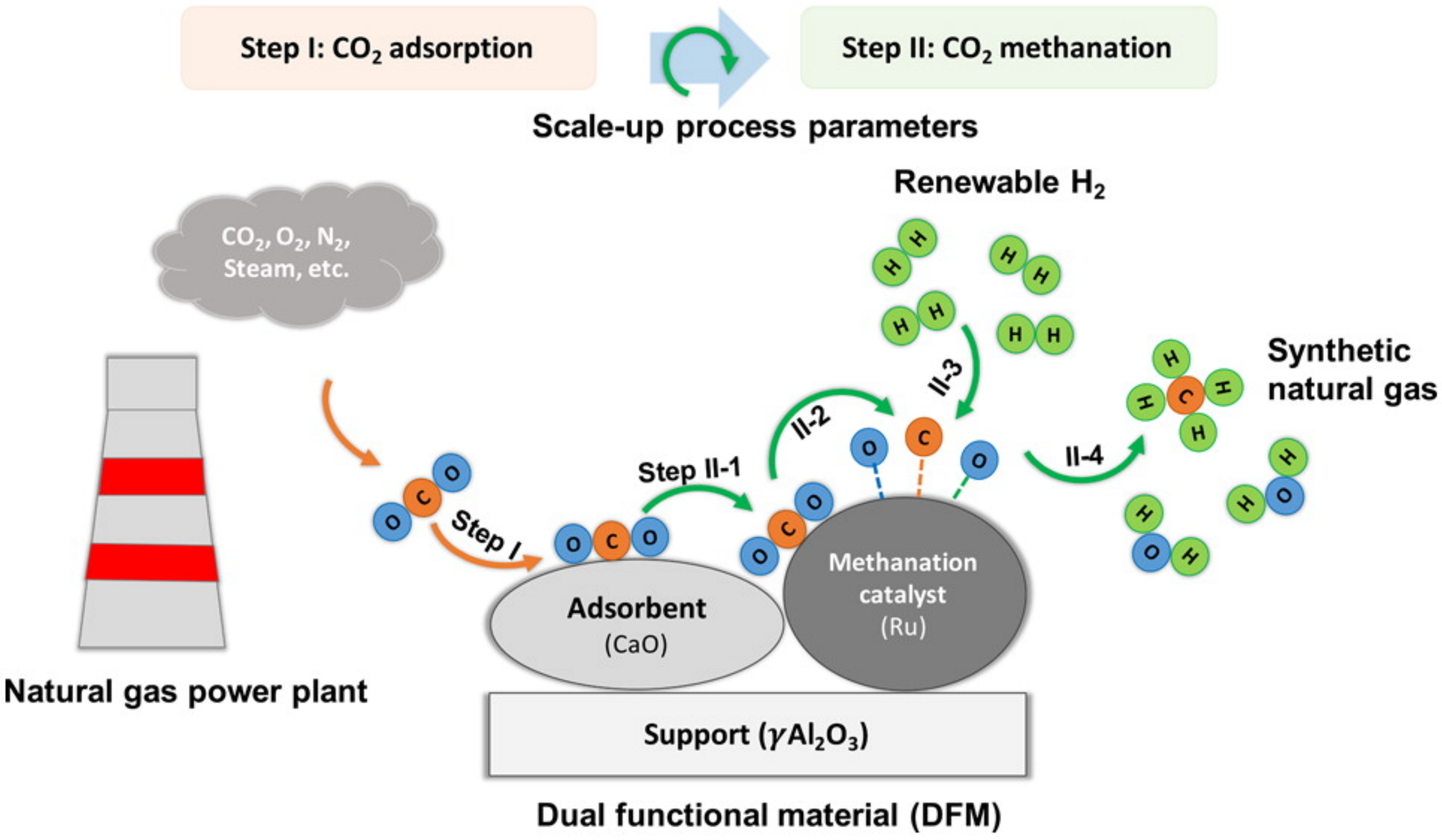
$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

$\Delta H_r°$= -165.0 kJ/mol

As the methanation reaction is exothermic, it allows for an efficient heat integration with the CO_2 desorption and spillover to the catalytic sites.

M.A. Arellano-Treviño, N. Kanani, C.W. Jeong-Potter, R.J. Farrauto; *Chem. Eng. J.* 375 **(2019)** 121953.

Dual-Function Materials for CO_2 Capture and Conversion



Q. Zheng, R.J. Farrauto, A.C. Nguyen; *Ind. Eng. Chem. Res.* 55 (24) **(2016)** 6768-6776.

Adsorbents for CO_2 Capture in DFMs

$$CaO\ (s) + CO_2\ (g) \rightleftharpoons CaCO_3\ (s); \quad \Delta H_r° = -178.2\ kJ/mol$$

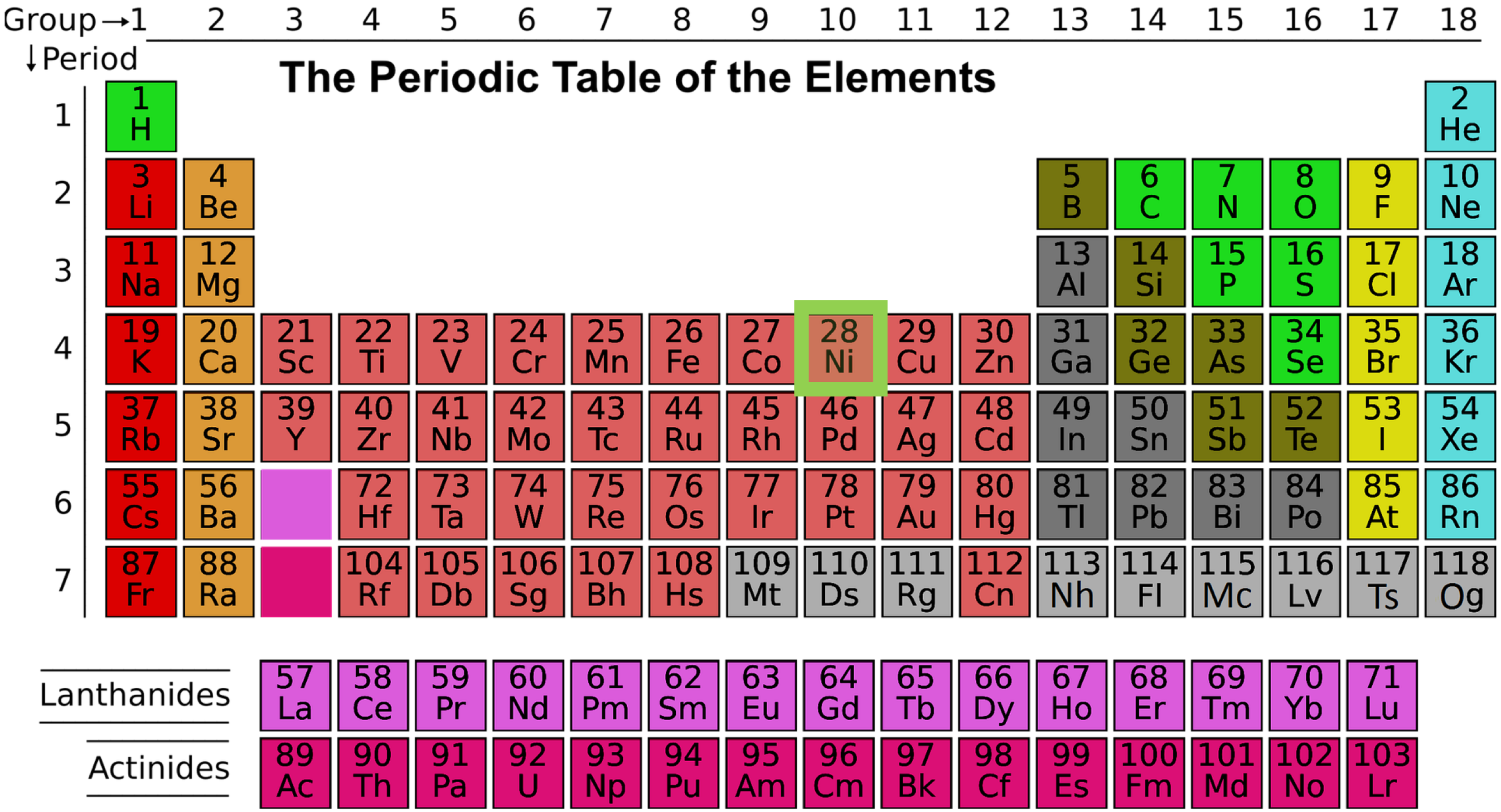
+ Inexpensive, robust, and highly reactive.
+ Energy-intensive regeneration often results in sintering.
- CaO carbonation is slow after forming the first layer of $CaCO_3$.

$$Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g) \rightleftharpoons 2NaHCO_3\ (s); \quad \Delta H_r° = -135\ kJ/mol$$

$$Na_2CO_3\ (s) + 0.6CO_2\ (g) + 0.6H_2O\ (g) \rightleftharpoons 0.4[Na_2CO_3 \cdot 3NaHCO_3]\ (s); \quad \Delta H_r° = -82\ kJ/mol$$

I.S. Omodolor, H.O. Otor, J.A. Andonegui, B.J. Allen, A.C. Alba-Rubio; *Ind. Eng. Chem. Res.* 59 (40) **(2020)** 17612-17631.

Catalytic Components in DFMs: Ni



Catalytic Components in DFMs: Ni

$$CO_2\ (g) + CH_4\ (g) \rightleftharpoons 2CO\ (g) + 2H_2\ (g); \quad \Delta H_r^\circ = +247.0\ kJ/mol$$

$$CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g); \quad \Delta H_r^\circ = +41.2\ kJ/mol$$

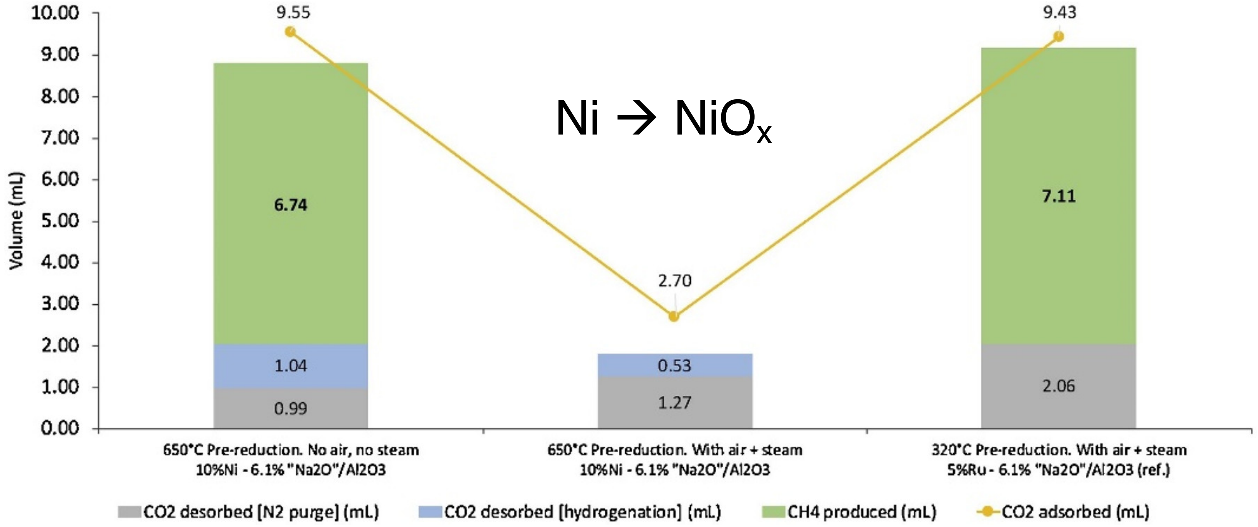
$$2CO_2\ (g) + C_2H_6\ (g) \rightleftharpoons 4CO\ (g) + 3H_2\ (g); \quad \Delta H_r^\circ = +428.1\ kJ/mol$$

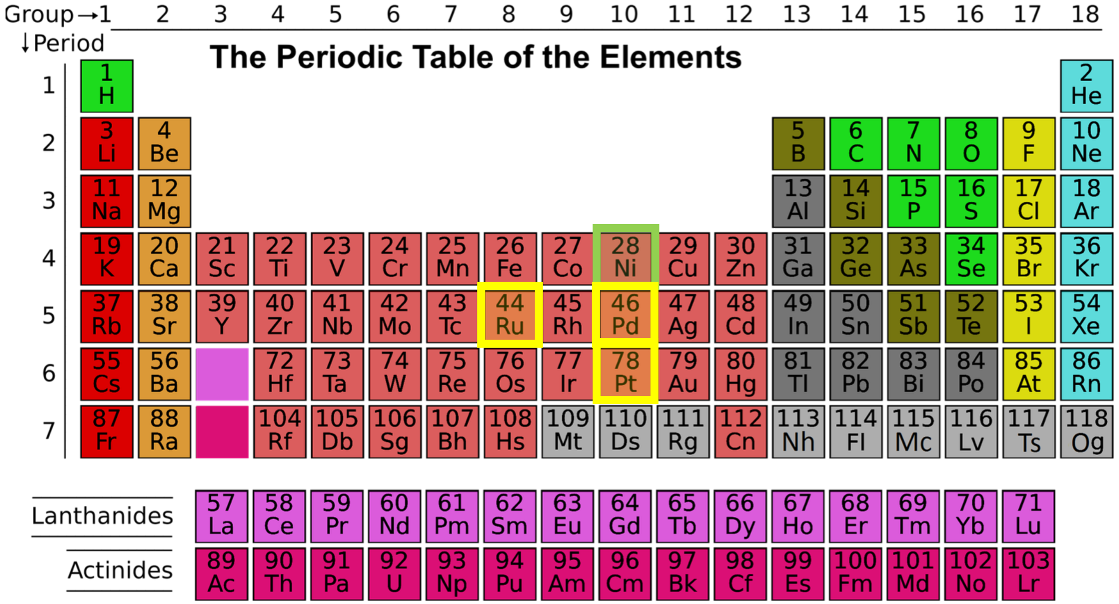
$$CO_2\ (g) + 4H_2\ (g) \rightleftharpoons CH_4\ (g) + 2H_2O\ (g); \quad \Delta H_r^\circ = -165.0\ kJ/mol$$

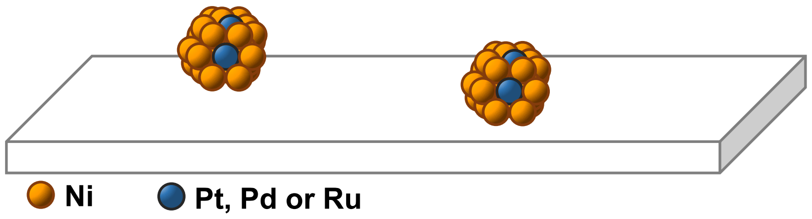
			Temperature (°C)		Feed composition	
DFM	**Synthesis method**	**Reaction**	**Adsorption**	**Reaction**	**Adsorption**	**Reaction**
Ni-CaO	Pechini sol–gel	DRM	600	800	CO_2	CH_4
CaO + Ni/MgO-Al_2O_3	Coprecipitation	DRM	720	720	20% CO_2/N_2	2.4% CH_4/N_2
Ni-CaO-Ce	Sol–gel combustion	RWGS	650–750	650–750	15% CO_2/N_2	5% H_2/N_2
Ni-(K–Ca)/γ-Al_2O_3	Wet impregnation	DER	650	650	10% CO_2/N_2	5% C_2H_6/N_2
Ni-(Na–Ca)/γ-Al_2O_3	Wet impregnation	DER	650	650	10% CO_2/N_2	5% C_2H_6/N_2
Ni-(K–Mg)/γ-Al_2O_3	Wet impregnation	DER	650	650	10% CO_2/N_2	5% C_2H_6/N_2
Ni-(Na–Mg)/γ-Al_2O_3	Wet impregnation	DER	650	650	10% CO_2/N_2	5% C_2H_6/N_2
Ni-CaO/Al_2O_3	Wet impregnation	Methanation	280–520	280–520	10% CO_2/Ar	10% H_2/Ar
Ni–Na_2CO_3/Al_2O_3	Wet impregnation	Methanation	280–520	280–520	10% CO_2/Ar	10% H_2/Ar
Ni–Na_2O/Al_2O_3	Incipient wetness impregnation	Methanation	320	320	7.5% CO_2/N_2 and 7.5% CO_2, 4.5% O_2, 15% H_2O/N_2	15% H_2/N_2

I.S. Omodolor, H.O. Otor, J.A. Andonegui, B.J. Allen, A.C. Alba-Rubio; *Ind. Eng. Chem. Res.* 59 (40) **(2020)** 17612-17631.

Catalytic Components in DFMs: Ni







The best results (CO_2 capture and CH_4 production) were obtained with a 1% Ru, 10% Ni, 6.1% Na_2O/Al_2O_3 DFM.

M.A. Arellano-Treviño, Z. He, M.C. Libby, R.J. Farrauto; *J. CO_2 Util.* 31 **(2019)** 143-151.
M.A. Arellano-Treviño, N. Kanani, C.W. Jeong-Potter, R.J. Farrauto; *Chem. Eng. J.* 375 **(2019)** 121953.

Catalytic Components in DFMs: Ru and Rh

The Periodic Table of the Elements

Group→ / ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

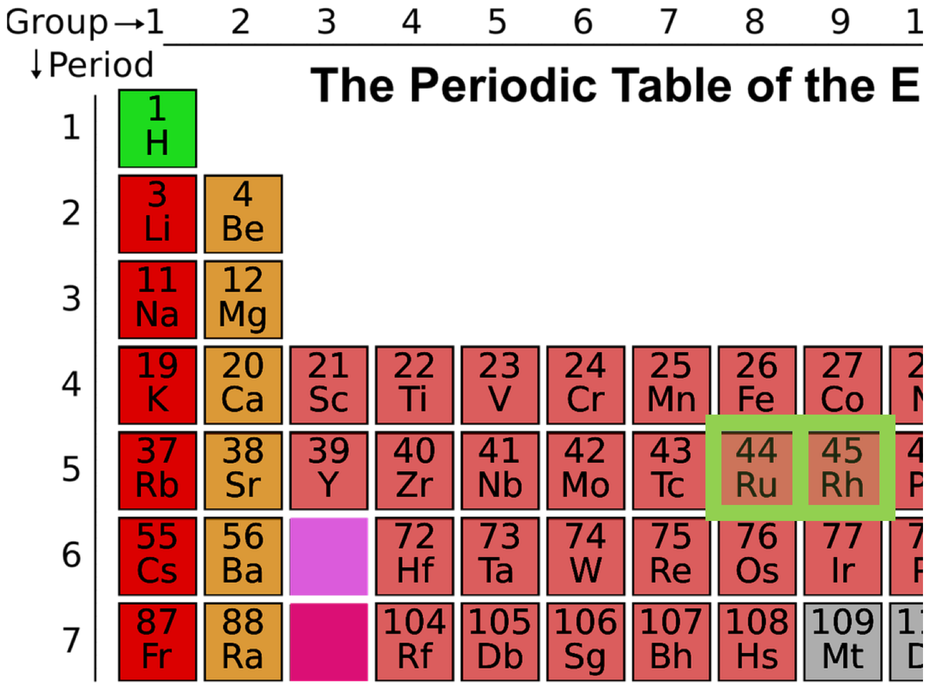
Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Catalytic Components in DFMs: Ru and Rh

			Temperature (°C)		Feed composition	
DFM	**Synthesis method**	**Reaction**	**Adsorption**	**Reaction**	**Adsorption**	**Reaction**
Ru-CaO/γ-Al_2O_3	Incipient wetness impregnation	Methanation	320	320	10% CO_2/air and 8% CO_2/21% H_2O/air	5% H_2/N_2
Ru-CaO/γ-Al_2O_3	Incipient wetness impregnation	Methanation	320	320	10% CO_2/N_2	4% H_2/N_2
Ru-CaO/γ-Al_2O_3	Incipient wetness impregnation	Methanation	320	320	7.5% CO_2, 4.5% O_2, 15% H_2O/N_2	5% H_2/ N_2
Ru–Na_2CO_3/γ-Al_2O_3	Incipient wetness impregnation	Methanation	320	320	7.5% CO_2/N_2 and 7.5% CO_2, 4.5% O_2, 15% H_2O/N_2	5% H_2/N_2
Ru–Na_2O/γ-Al_2O_3	Incipient wetness impregnation	Methanation	250–350	250–350	7.5% CO_2, 4.5% O_2, 15% H_2O/N_2	15% H_2/N_2
Ru-CaO/γ-Al_2O_3	Incipient wetness impregnation	Methanation	280–400	280–400	1.4% CO_2/Ar and 11% CO_2/Ar	10% H_2/Ar
Ru–Na_2CO_3/γ-Al_2O_3	Incipient wetness impregnation	Methanation	280–400	280–400	1.4% CO_2/Ar and 11% CO_2/Ar	10% H_2/Ar
Ru–Na_2O/γ-Al_2O_3	Incipient wetness impregnation	Methanation	320	320	15% CO_2/N_2	20% H_2/N_2
Rh-CaO/γ-Al_2O_3	Incipient wetness impregnation	Methanation	320	320	10% CO_2/N_2	2% H_2/N_2
Ru-CaO/γ-Al_2O_3	Incipient wetness impregnation	Methanation	320	320	10% CO_2/air and 8% CO_2/21% H_2O/air	5% H_2/N_2

I.S. Omodolor, H.O. Otor, J.A. Andonegui, B.J. Allen, A.C. Alba-Rubio; *Ind. Eng. Chem. Res.* 59 (40) **(2020)** 17612-17631.

Catalytic Components in DFMs: Ru and Rh



Sample	mol CH_4/mol Ru	mol CH_4/kg DFM
γ-Al_2O_3	0	0.00
10% Ru/γ-Al_2O_3	0.1	0.10
1% CaO, 10% Ru/γ-Al_2O_3	0.19	0.19
5% CaO, 10% Ru/γ-Al_2O_3	0.27	0.27
10% CaO, 10% Ru/γ-Al_2O_3	0.31	0.30
1.1% Ru, 10% CaO/γ-Al_2O_3	2.46	0.27
2% Ru, 10% CaO/γ-Al_2O_3	1.79	0.35
5% Ru, 10% CaO/γ-Al_2O_3	1.01	0.50
6.8% Ru, 10% CaO/γ-Al_2O_3	0.65	0.44
10.6% Ru, 10% CaO/γ-Al_2O_3	0.44	0.46
10% Ru/γ-Al_2O_3 + 10% CaO/γ-Al_2O_3	0.25	0.12

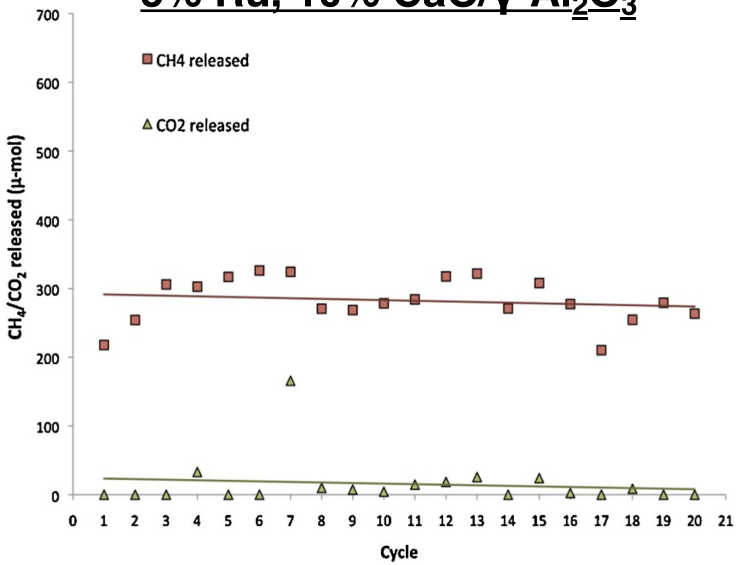
Better: 1) sorbent and 2) catalyst → increased Ru dispersion without coverage of the active sites by CaO.

CaO improved the methanation rate (even when physically mixed) → spillover of CO_2 from CaO sites to the Ru sites during hydrogenation.

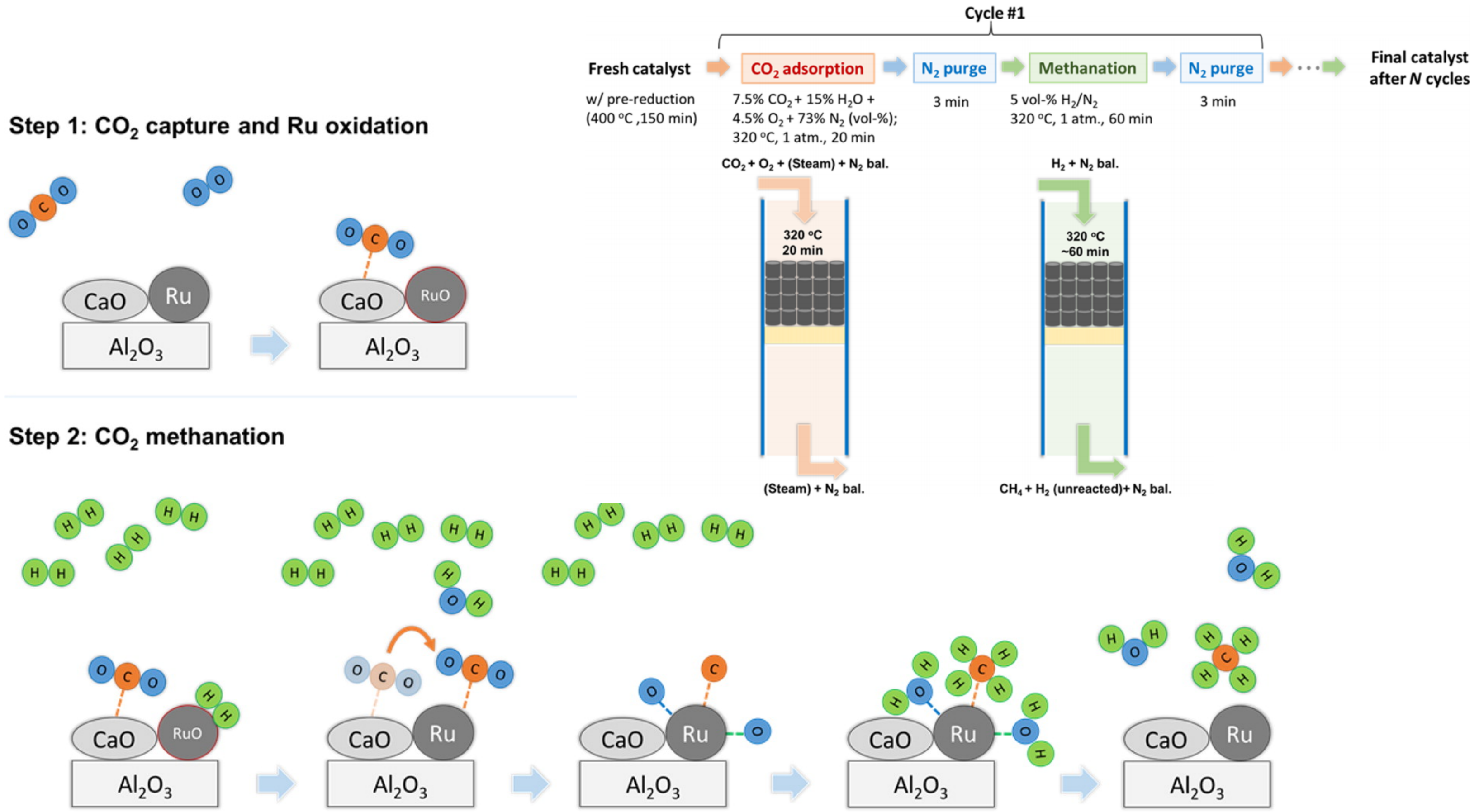
M.S. Duyar, M.A. Arellano-Treviño, R.J. Farrauto; *Appl. Catal., B 168-169* **(2015)** 370-376.

Catalytic Components in DFMs: Ru and Rh

5% Ru, 10% $CaO/\gamma\text{-}Al_2O_3$



The presence of water and oxygen reduced the adsorption and conversion capacity due to the oxidation of the Ru species.



M.S. Duyar, M.A. Arellano-Treviño, R.J. Farrauto; *Appl. Catal., B* 168-169 **(2015)** 370-376.
Q. Zheng, R.J. Farrauto, A.C. Nguyen*; Ind. Eng. Chem. Res.* 55 (24) **(2016)** 6768-6776.

Catalytic Components in DFMs: Ru and Rh

The higher adsorptive capacity of the sorbent species, the more effective the DFM is:

$Na_2CO_3 > K_2CO_3 > CaO$

Sample	mol CH_4/kg DFM
5% Ru, 10% CaO/γ-Al_2O_3	0.50
5% Ru, 10% K_2CO_3/γ-Al_2O_3	0.91
5% Ru, 10% Na_2CO_3/γ-Al_2O_3	1.05

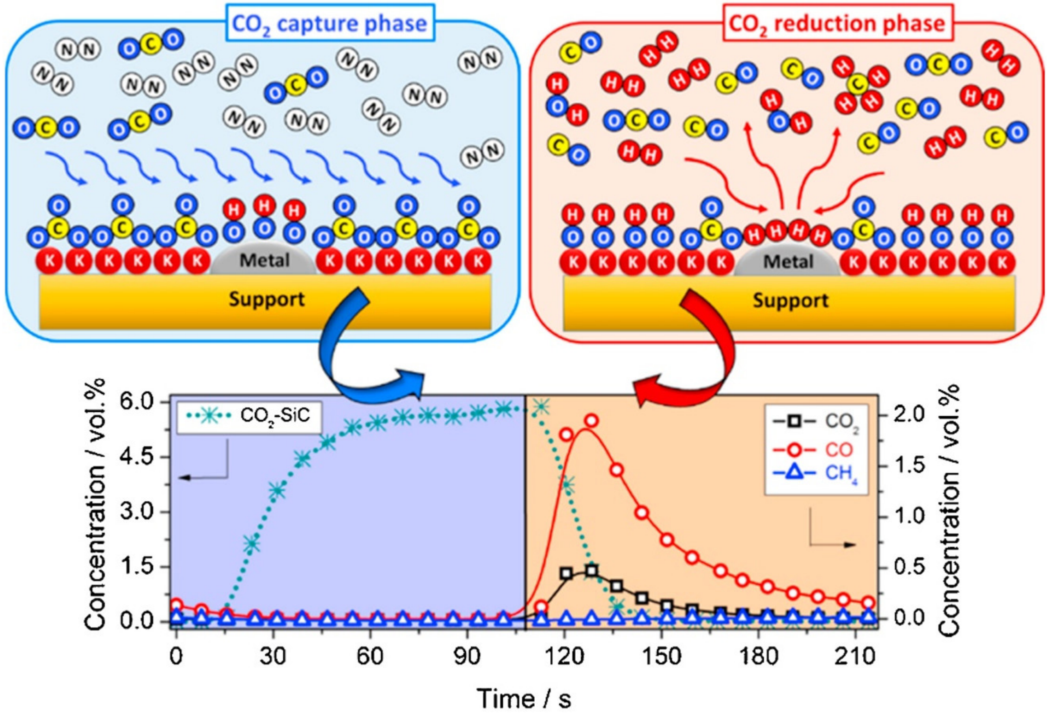
Sample	mol CH_4/mol Rh or Ru	mol CH_4/kg DFM
10% Rh/γ-Al_2O_3	0.3	0.30
10% Rh, 10% CaO/γ-Al_2O_3	0.9	0.90
5% Rh, 10% CaO/γ-Al_2O_3	1.3	0.70
1% Rh, 10% CaO/γ-Al_2O_3	7.0	0.70
0.1% Rh, 10% CaO/γ-Al_2O_3	42.0	0.40
5% Ru, 10% CaO/γ-Al_2O_3	1.0	0.50

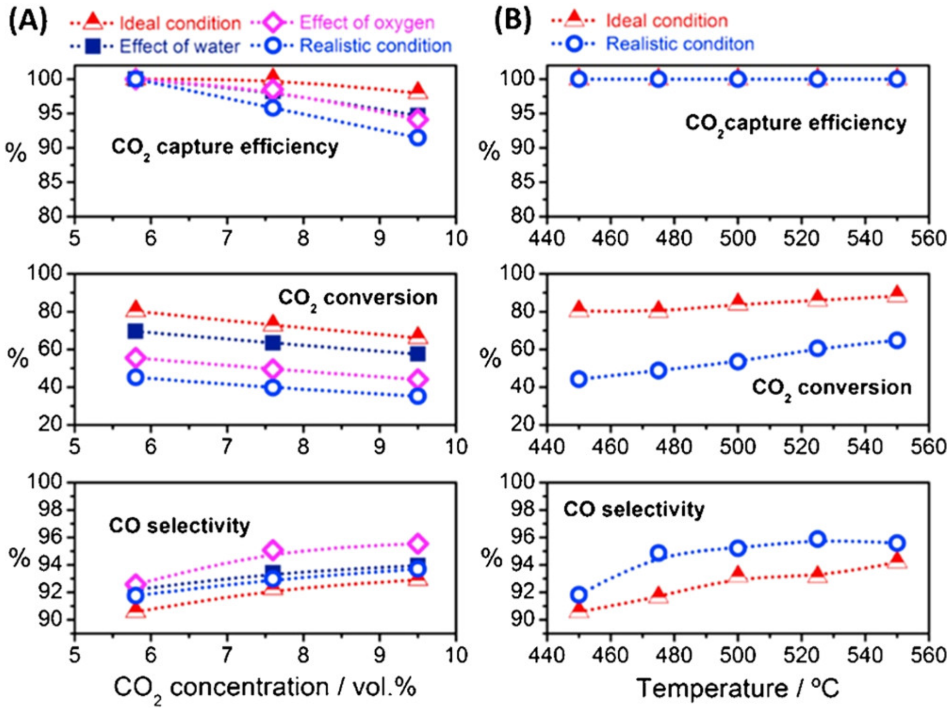
Ru: $365/troy oz.
Rh: $28,850/troy oz!

M.S. Duyar, S. Wang, M.A. Arellano-Treviño, R.J. Farrauto; *J. CO_2 Util.* 15 **(2016)** 65-71.

DFMs with Non-Noble Metals

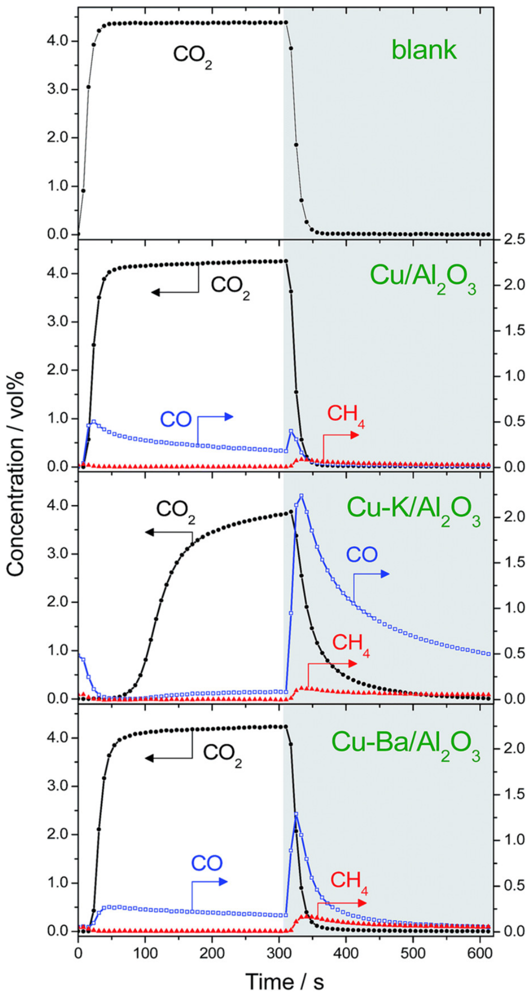
CO_2 conversion to syngas: CO_2 is adsorbed over the alkali metal (K) forming surface carbonates, and after switching to H_2, most of the captured CO_2 reacts with H_2 over the catalytic sites (Fe, Cu, and Cr). Exceptional stability after 750 capture/reduction cycles (45 h).





L.F. Bobadilla, J.M. Riesco-Garcia, G. Penelas-Perez, A. Urakawa; *J. CO_2 Util.* 14 **(2016)** 106-111.

DFMs with Non-Noble Metals



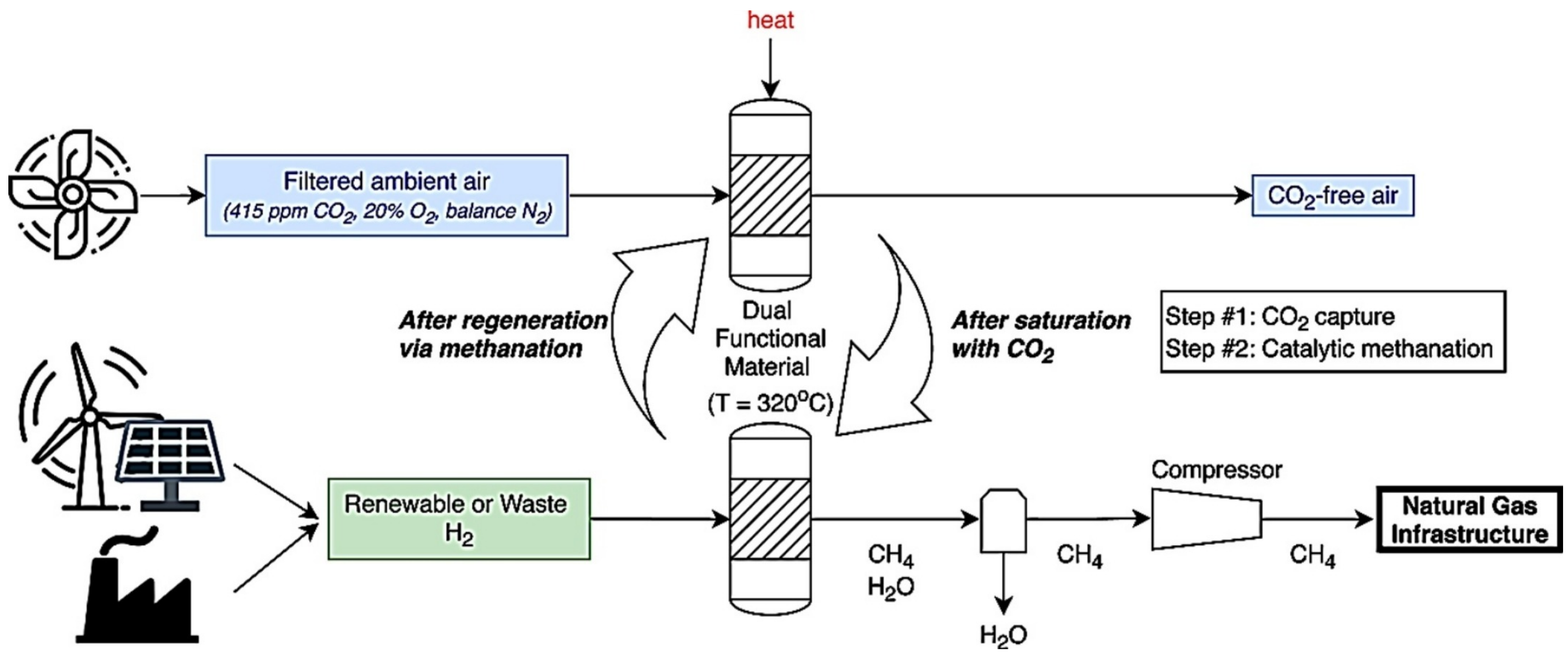
CO_2 capture and conversion at 350 °C using 4.4% CO_2/He and pure H_2, respectively.

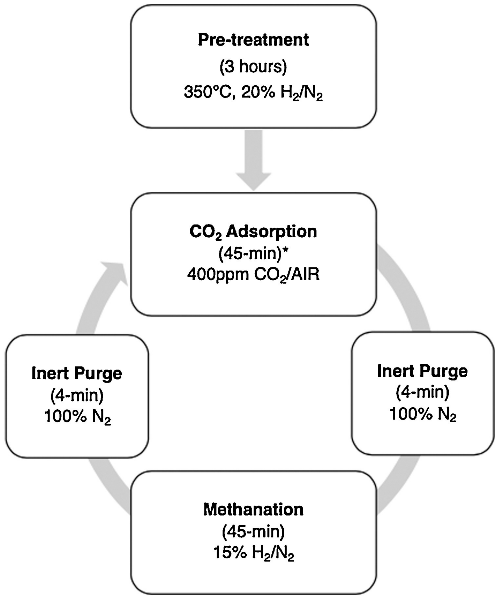
Cu/Al_2O_3: Mostly produced CO during capture step, which was attributed to the surface oxidation of Cu.
Cu-K/Al_2O_3: capturing CO_2 as formate species and subsequently converting them into CO upon exposure to H_2.
Cu-Ba/Al_2O_3: Mixed behavior with CO formed during capture and conversion. Did not fully captured CO_2.

XAFS studies showed that Cu remained free from oxidation on Cu-K/Al_2O_3. DRIFTS confirmed the presence of formate species, which is an intermediate commonly reported for CO and methanol formation.

T. Hyakutake, W. van Beek, A. Urakawa; *J. Mater. Chem. A* 4 (18) **(2016)** 6878-6885.

Feasibility of Direct Air Capture (DAC) with DFMs

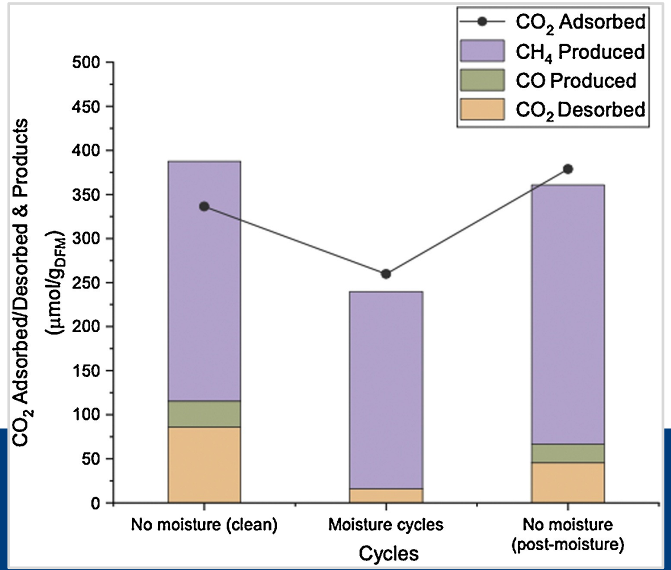




<u>0.5% Ru, 6.1% Na_2O/Al_2O_3</u>
200 mmol CO_2/kg_{DFM} and 150 mmol CH_4/kg_{DFM}

Even after exposure to O_2 during the capture step, the Ru component of the DFM is rapidly and completely reactivated for catalytic conversion.

C. Jeong-Potter, R. Farrauto; *Appl. Catal. B* 282 **(2021)** 119416.



Al Ba-Ru Bi O group

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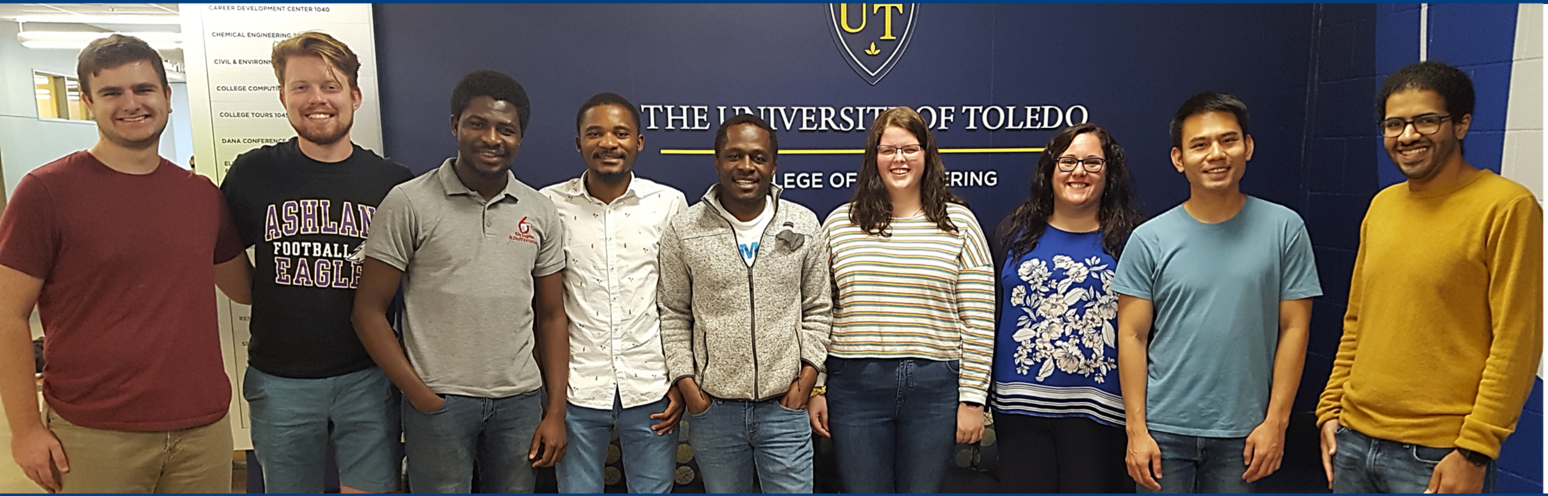

Bryan Allen, Josh Steiner, Hope Otor, Kapiamba Fabrice, Ibeh Omodolor, Sarah Walz, Ray Duanghathaipornsuk, Haidar Alolaywi

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THANK YOU!

Godfred Owusu

Caleb Hiddleson

Sridhar Viamajala