$SrTiO_3$ and $SrTiO_3$-based composites for photocatalytic CO_2 hydrogenation

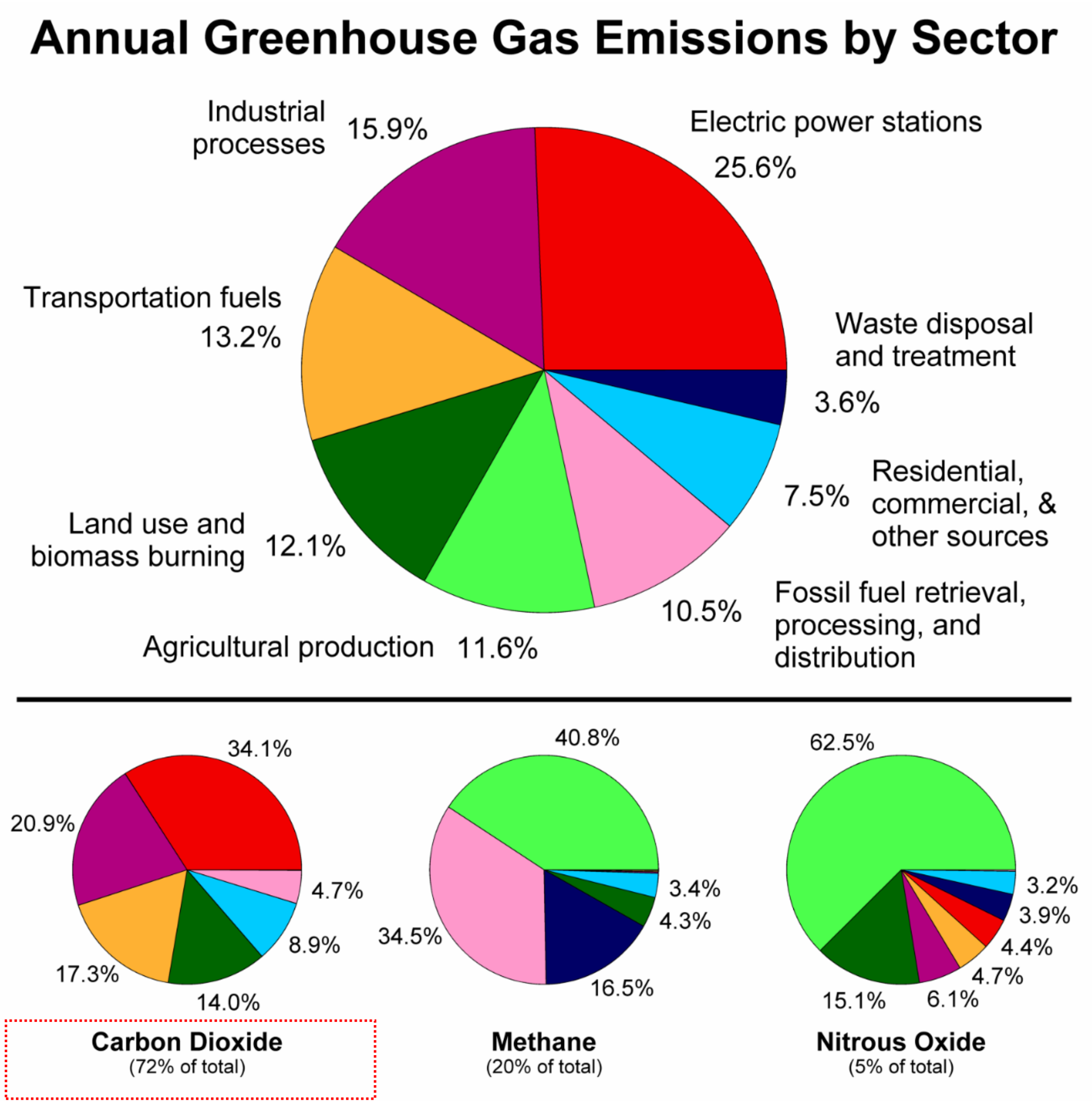
Dr. Mohit Yadav
Postdoctoral fellow
Department of Applied and Environmental chemistry
University of Szeged

Dr. Andras Sapi (Supervisor)
Assistant Professor
Department of Applied and Environmental Chemistry
University of Szeged, Hungary

Presentation outline

- **Background of study and Research scope**
- **Outline of the Project**
- **Specifications of the photocatalytic reactor**
- **Characterization results**
- **Photocatalytic results and discussion**
- **Major conclusions**
- **Future work**

Background and research scope

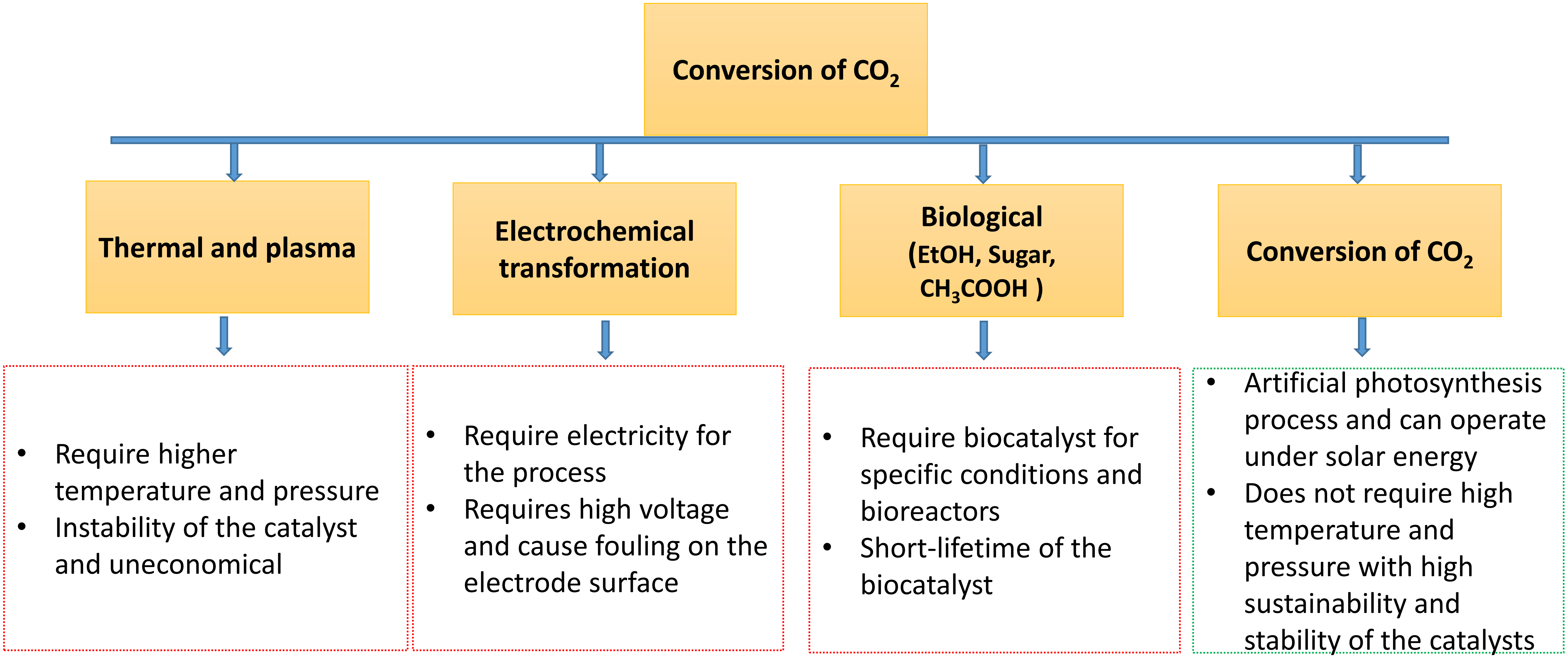


Major contributor

- Energy consumption has been increasing with the world population
- Fossil fuels are the main source of energy supply
- Combustion of fossil fuels generates greenhouse CO_2

Background and research scope

Recycling of CO_2 to fuels



Outline of the Project

I

Optimization of the $SrTiO_3$ (STO) based on
crystallization time
crystallization media
purification issues

STO-I
STO-II
STO-III
STO-IV
STO-V
STO-VI
STO-VII

II

Noble metals
(X= Rh, Ru and Pt)

- Noble metals effectively facilitates the **surface plasmon resonance (SPR)** for trapping electrons and boost the reduction potential of neighboring metal oxide .
- Also, trapping CO_2 in the **Carboxyl, carbonates, formates**, which are key intermediates towards the products.

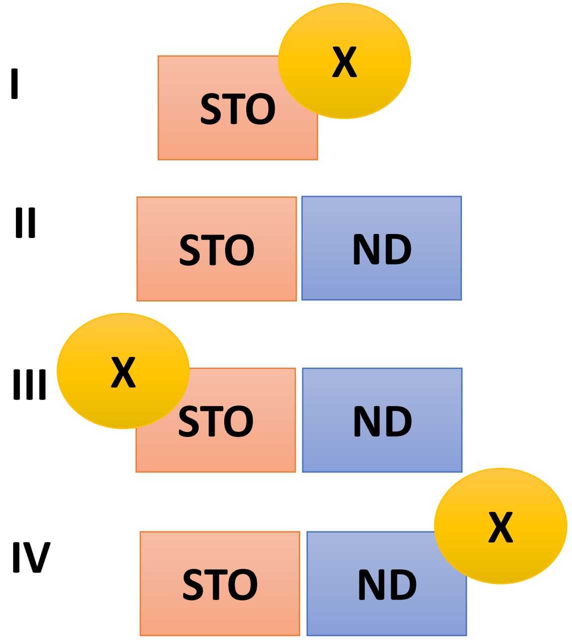
III

Nanodiamonds (NDs)

- A form of carbon nanomaterials, possess **excellent catalytic properties** because of its unique crystalline phase comprising of **sp^2 hybrid graphite and sp^3 diamond core**.
- Smaller particle sizes (**4–5 nm**) and high specific surface area (**~ 300 m^2 g^{-1}**)
- Upon coupling of NDs with the metal oxides formation of **heterojunction** takes place that efficiently facilitates the **charge transfer mechanism** and **separation of the electron-hole pairs**

IV

Sequential Deposition of Noble metals (X) and NDs on STO



Specifications and reaction conditions of the photocatalytic reactor system

- HP 5890 Series II Gas Chromatograph
- Light source: 500 W mercury vapor lamp (TQ 718, Heraeus Noble light, Germany)
- Weight of sample used: 250-300 mg
- Pressure (CO_2+H_2) : 200 mbar, Flow = 15 mL/min
- Column used: A 2 meter long column packed with Porapak QS

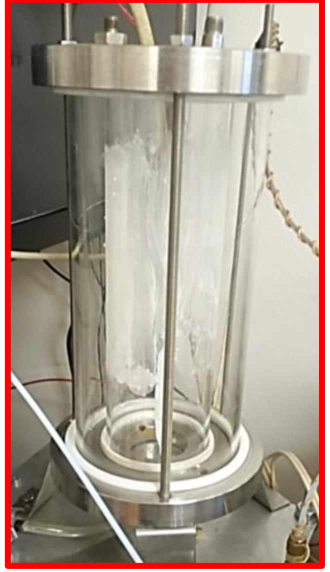
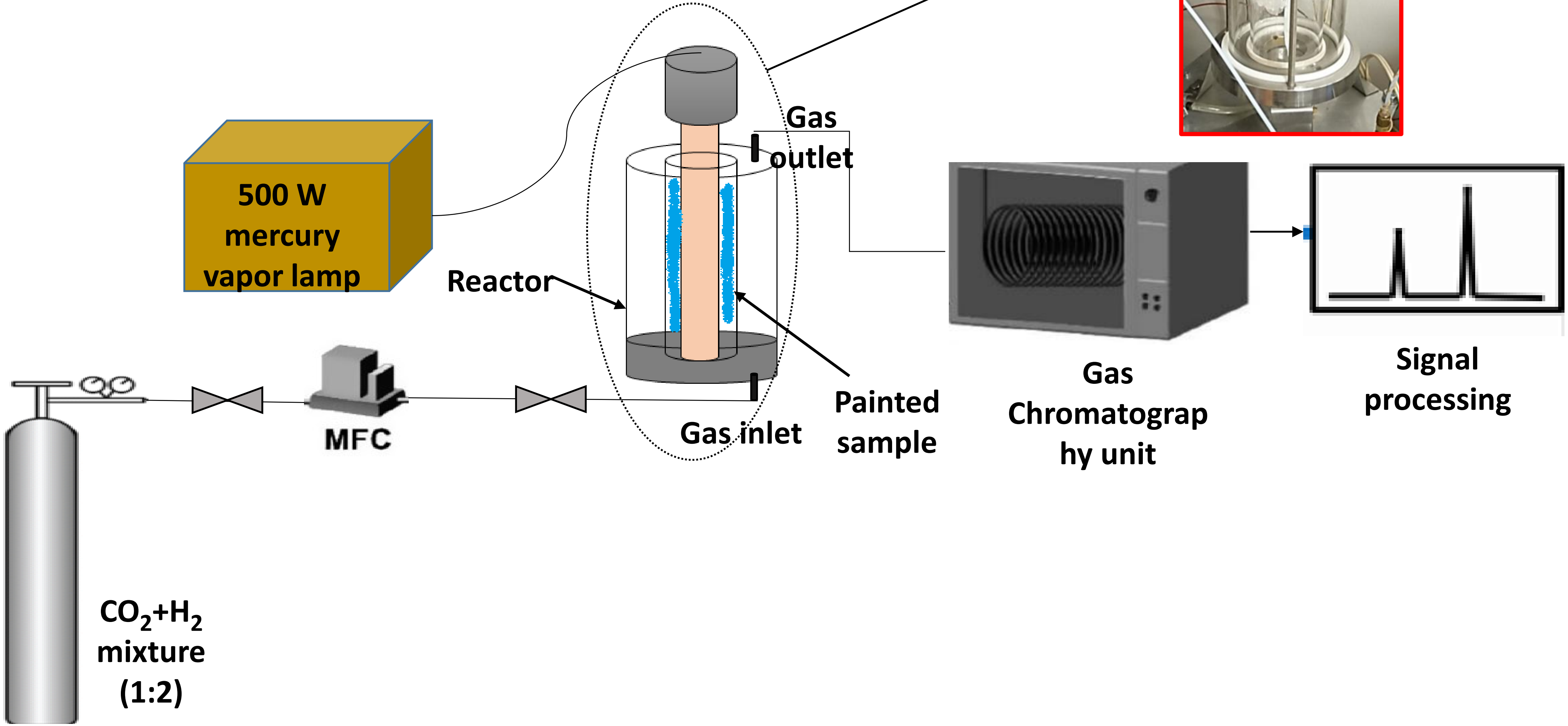
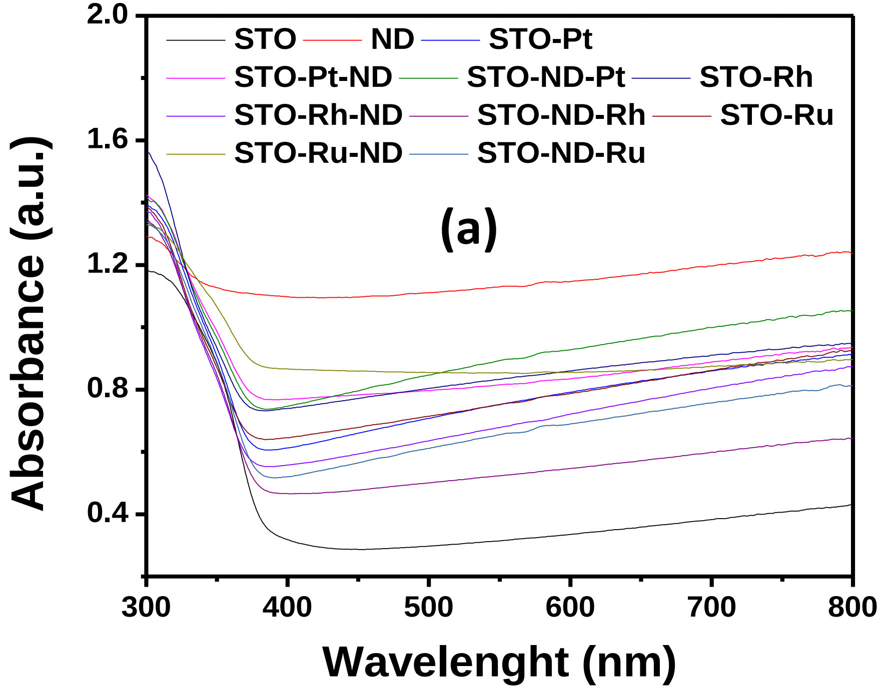


Image of the Reactor



Characterization



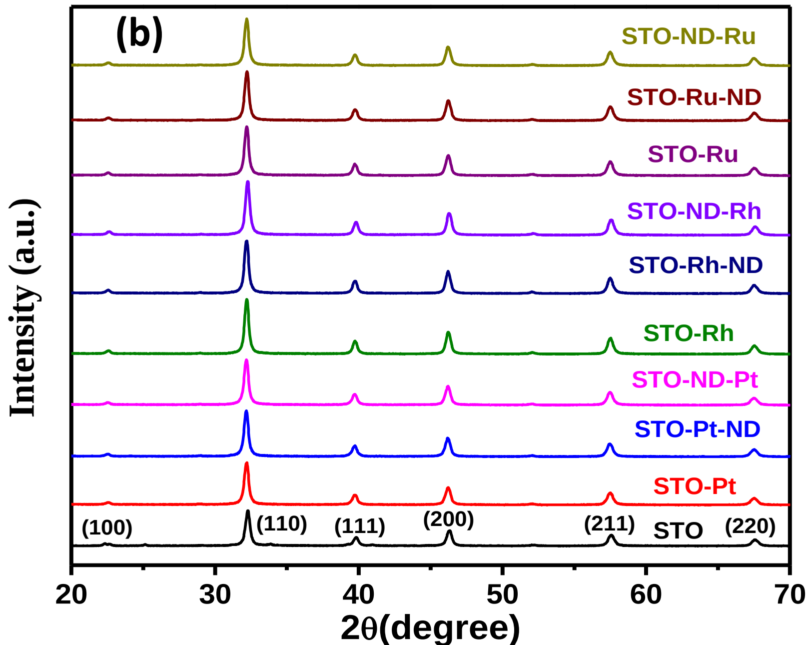
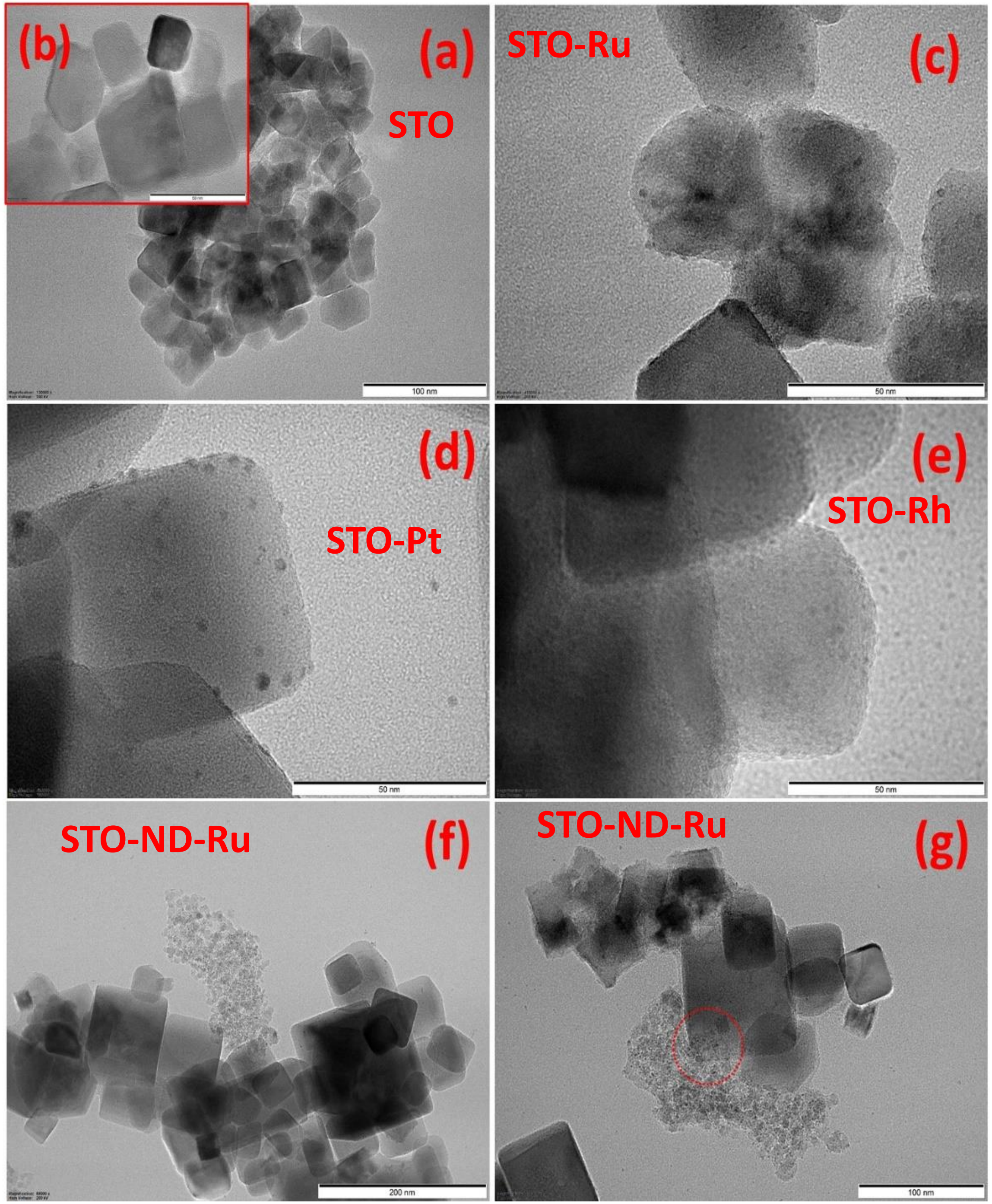


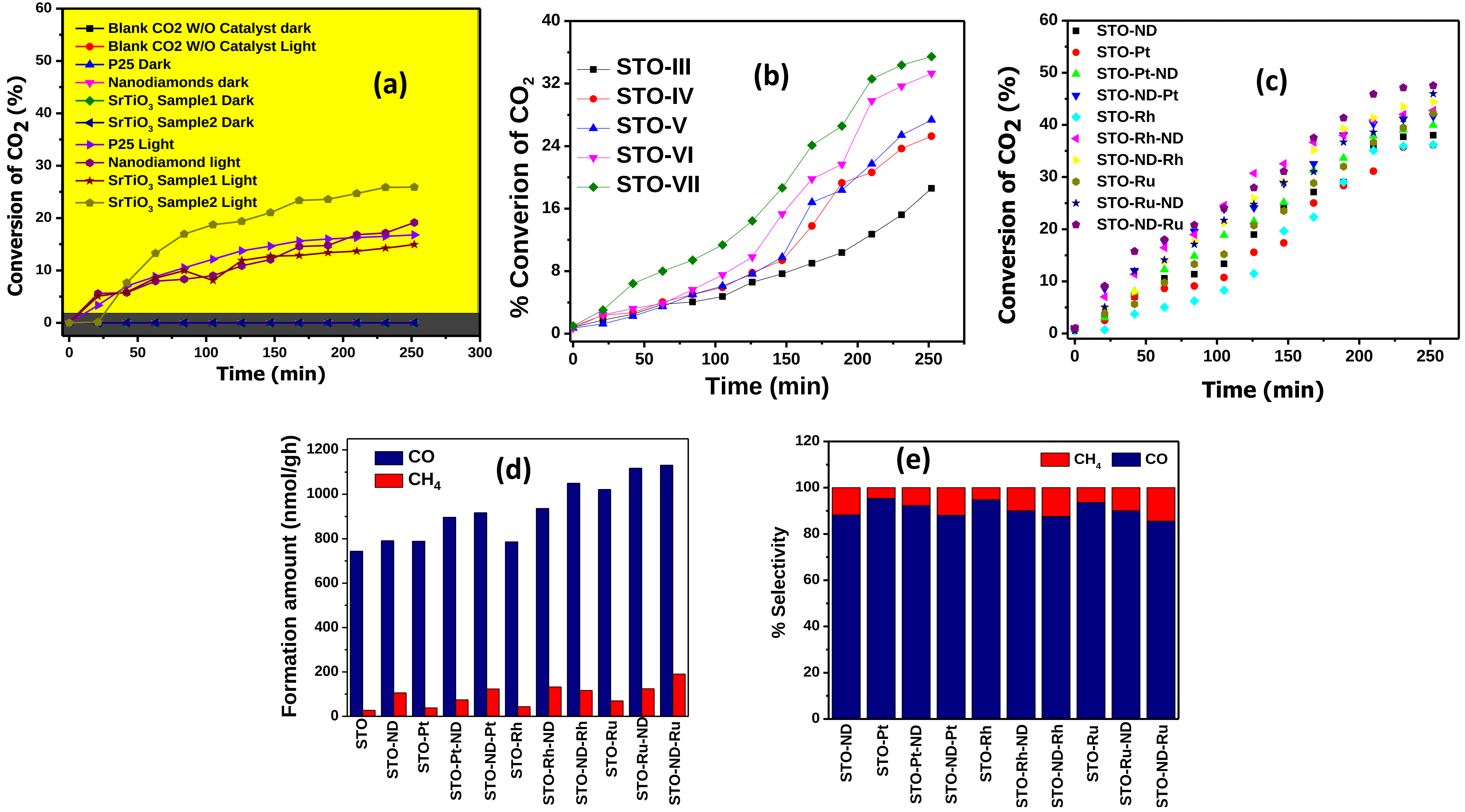
Table. Catalyst loadings along with BET surface areas, Band gap and primary crystallite size values.

Sample	Rh, Ru and Pt (wt%)	ND (wt%)	S.S.A ($m^2 g^{-1}$)	Band Gap (eV)	Primary crystallite size (nm)
STO	-	-	51.8	3.28	19.3
ND	-	-	302.5	2.88	3.59
STO-Pt	1	-	52.7	3.24	19.53
STO-Pt-ND	1	10	71.8	3.22	20.7
STO-ND-Pt	1	10	72.1	3.16	20.78
STO-Rh	1	-	53.7	3.26	19.34
STO-Rh-ND	1	10	69.7	3.25	20.24
STO-ND-Rh	1	10	72.3	3.17	20.4
STO-Ru	1	-	52.9	3.23	19.31
STO-Ru-ND	1	10	70.9	3.2	19.98
STO-ND-Ru	1	10	73.8	3.08	20.23

Characterization

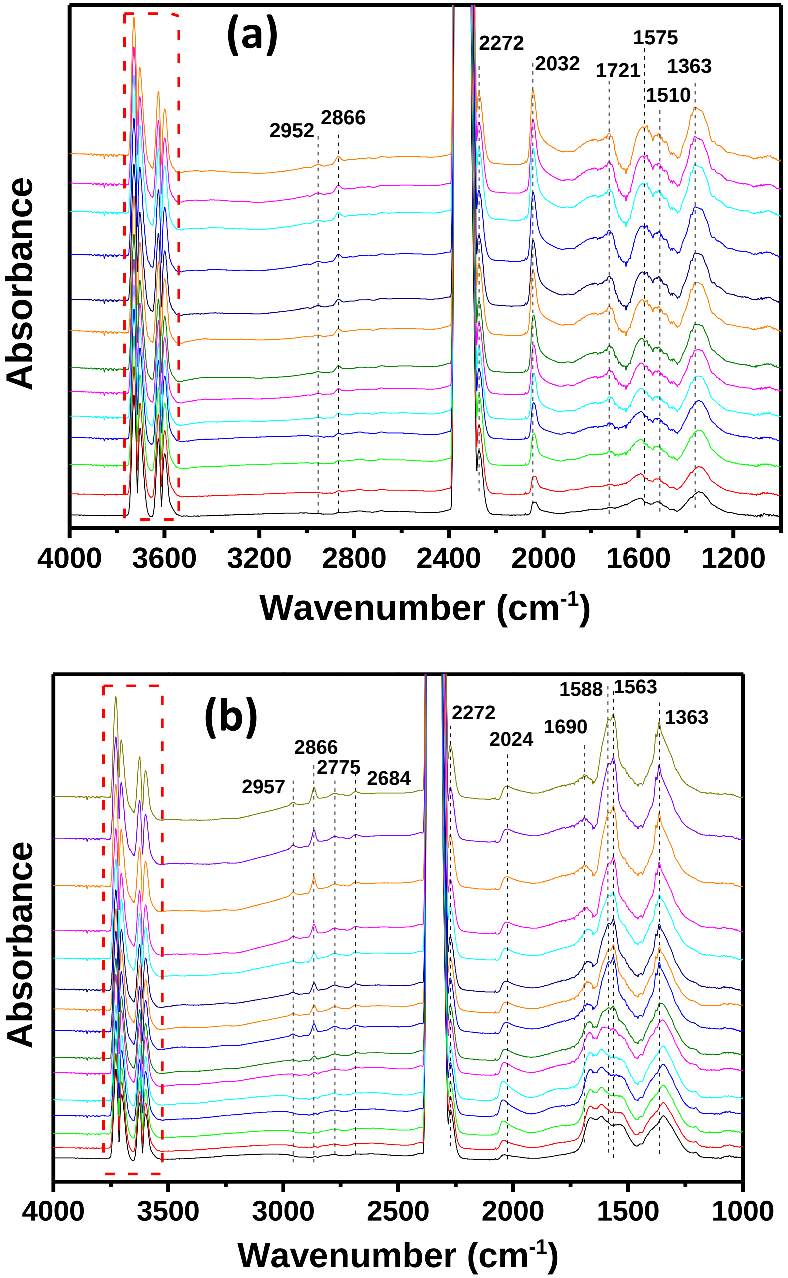
TEM images of the samples




(a)
Blank CO2 W/O Catalyst dark
Blank CO2 W/O Catalyst Light
P25 Dark
Nanodiamonds dark
SrTiO3 Sample1 Dark
SrTiO3 Sample2 Dark
P25 Light
Nanodiamond light
SrTiO3 Sample1 Light
SrTiO3 Sample2 Light
Conversion of CO2 (%)
Time (min)
(b)
STO-III
STO-IV
STO-V
STO-VI
STO-VII
% Converion of CO2
Time (min)
(c)
STO-ND
STO-Pt
STO-Pt-ND
STO-ND-Pt
STO-Rh
STO-Rh-ND
STO-ND-Rh
STO-Ru
STO-Ru-ND
STO-ND-Ru
Conversion of CO2 (%)
Time (min)
(d)
CO
CH4
Formation amount (nmol/gh)
STO
STO-ND
STO-Pt
STO-Pt-ND
STO-ND-Pt
STO-Rh
STO-Rh-ND
STO-ND-Rh
STO-Ru
STO-Ru-ND
STO-ND-Ru
(e)
CH4
CO
% Selectivity
STO-ND
STO-Pt
STO-Pt-ND
STO-ND-Pt
STO-Rh
STO-Rh-ND
STO-ND-Rh
STO-Ru
STO-Ru-ND
STO-ND-Ru

Samples	**% CO_2 conversion**	**Formation of products (nmol/gh)**		**Selectivity (%)**	
		CO	**CH_4**	**CO**	**CH_4**
STO	35.5	744.8	27.1	96.5	3.5
STO-ND	38.1	790.5	105.4	88.2	11.8
STO-Pt	36.1	788.1	38.3	95.4	4.6
STO-Pt-ND	39.9	896.7	74.5	92.3	7.7
STO-ND-Pt	41.6	917.3	123.8	88.1	11.9
STO-Rh	36.2	786.4	43.5	94.8	5.2
STO-Rh-ND	42.8	936.1	132.2	90.1	9.9
STO-ND-Rh	44.4	1050.7	116.4	87.6	12.4
STO-Ru	42.3	1022.4	69.3	93.6	6.4
STO-Ru-ND	45.9	1117.1	124.4	89.9	10.1
STO-ND-Ru	**47.5**	**1131.5**	**190.3**	**85.6**	**14.4**

DRIFTS measurements for the optimized STO-Ru-ND and STO-ND-Ru samples



STO-Ru-ND		STO-ND-Ru	
Wavenumber (cm^{-1})	Species	Wavenumber (cm^{-1})	Species
3000-3700	Hydroxyl region	3000-3700	Hydroxyl region
2400-2200	CO_2	2400-2200	CO_2
2024, 2272	Linearly adsorbed CO_{ad}	2032, 2272	Linearly adsorbed CO_{ad}
1690, 1662	Carboxylic acid		Carboxyl
2957, 2775, 2684, 2866, 1588, 1363	Bridged Formate	2952, 286, 1575, 1363	Bridged Formate
1563	Bidentate carbonate	-	Bidentate carbonate
-	Bridged carbonate	1721	Bridged carbonate
-	Inorganic carboxylate	1510	Inorganic carboxylate

Major Conclusions

Optimization of STO samples on the basis of certain factors followed by sequential deposition of noble metals and NDs was carried out and were tested for photocatalytic CO_2 hydrogenation.

The light absorption properties and the specific surface areas were enhanced with the deposition of noble metals and NDs.

The selective deposition also directly effected the formation and selectivity of the products i.e., ND directly attached to STO enhanced the formation of CH_4, however, deposition of Noble metals with produced mostly CO with little amount of CH_4.

Overall the photocatalytic activity was enhanced with deposition of both noble metals and ND, and STO-ND-Ru showed the highest activity and formation rate for the products.

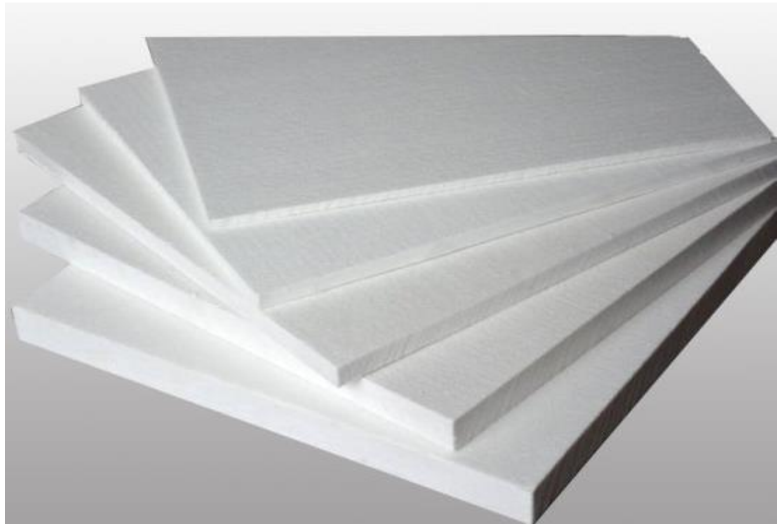
Future Plans

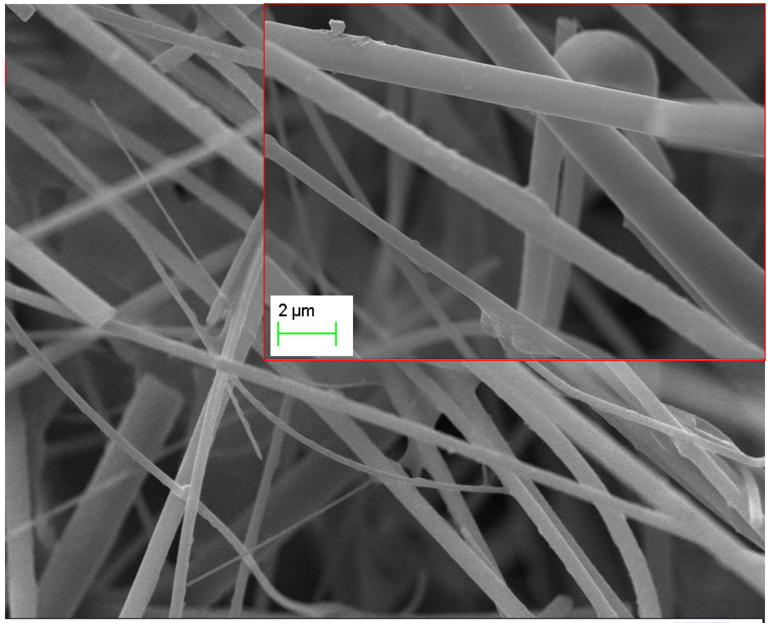
Near Future

- Finish the pending manuscripts
- Complete the Croatian project and manuscript writing

Long term

- The applied ceramic fiber sheet is Al_2O_3-based, non-woven, 1.6 mm thick and highly flexible paper(Catalog No. 300-040-1).
- With the immobilization of the photocatalyst on the ceramic sheet, loss of photocatalyst can be avoided.
- It can be used multiple times with same efficiency.





Thank you!