Ammonia synthesis using non-thermal plasma with Ru-based catalysts

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Introduction

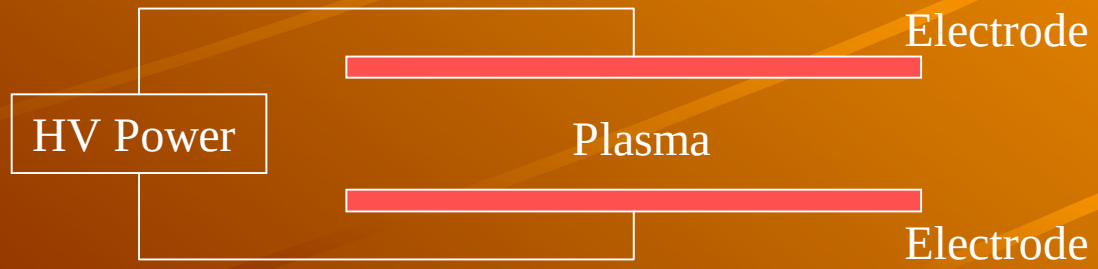
- Ammonia is one of the most valuable industrial chemicals and agricultural fertilizer. More recently it is considered as a direct fuel or hydrogen carrier.
- Traditionally ammonia is synthesized from hydrogen and nitrogen gases under high pressure and temperature with the help of catalysts. This process (Haber process) is usually carried out in large scales.
- There is a clear need for a more active catalytic system or a new route for ammonia synthesis at milder operating conditions to address the interest of smaller distributed ammonia production systems, to fully and more efficiently utilized the wind energy, for example.

Objectives

- Develop efficient non-thermal plasma (NTP) systems for synthesis of NH_3 from renewable hydrogen such as wind hydrogen.
- Evaluate different catalysts and promoters and the synergy effect with non-thermal plasma.
- Study NTP processing parameters such as applied voltage, frequency, gas ratio, and residence time.

What is NTP?

- NTP species include: energetic electrons, photons, atoms, and molecules, highly reactive radicals, ozone, etc. Ozone is the most widely used NTP species.
- NTP is generated though electrical discharge in gas (in atmosphere or liquid).



Nonthermal Plasma (NTP)

Generation of highly reactive species

$e + O_2 \longrightarrow O_2^+ + 2e$

$O^+ + O + 2e$

$O^* + O + e$

$O^- + O$

$e + N_2 \longrightarrow N_2^+ + 2e$

$N^+ + N + 2e$

$N_2^* + e$

$N^* + N + e$

$O^* + H_2O \longrightarrow 2OH$

$O + O_2 + O_2 \longrightarrow O_3 + O_2$

$e + H_2O \longrightarrow H + OH$

Effects of NTP on gaseous compounds

$NO_x + O$	$\longrightarrow$	NO or NO_2
$NO_x + OH$	$\longrightarrow$	HNO_3
$NO_x + N$	$\longrightarrow$	$N_2 + O_2$
$SO_x + O + H_2O$	$\longrightarrow$	H_2SO_4
$SO_x + 2OH$	$\longrightarrow$	H_2SO_4
$NH_3 + O$	$\longrightarrow$	$N_2 + H_2O$
$H_2S + OH$	$\longrightarrow$	$SO_2 + H_2O$
$CO_x + O$	$\longrightarrow$	$CO_2 + CO$

Effects of NTP on gaseous compounds

$$\_O + VOCs \longrightarrow CO_x + H_2O + byproducts$$

$$\_OH + VOCs \longrightarrow CO_x + H_2O + byproducts$$

$$\_O_3 + VOCs \longrightarrow CO_x + H_2O + byproducts$$

$$e + O_2 + VOCs \longrightarrow CO_x + H_2O + byproducts$$

depending on VOCs

Pulsed Corona Discharge Reactors

Silent discharge reactors

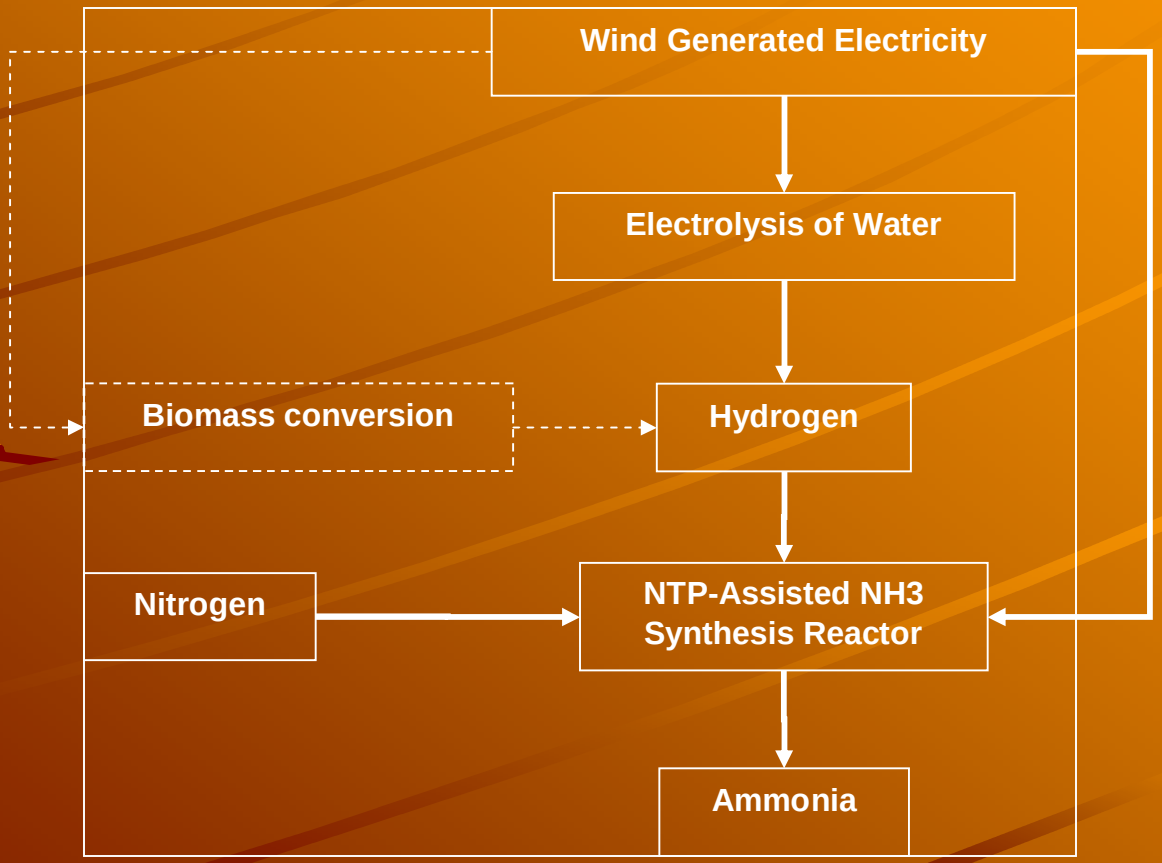
NTP Reactors

Packed-Bed NTP reactor

Pilot NTP surface disinfection system

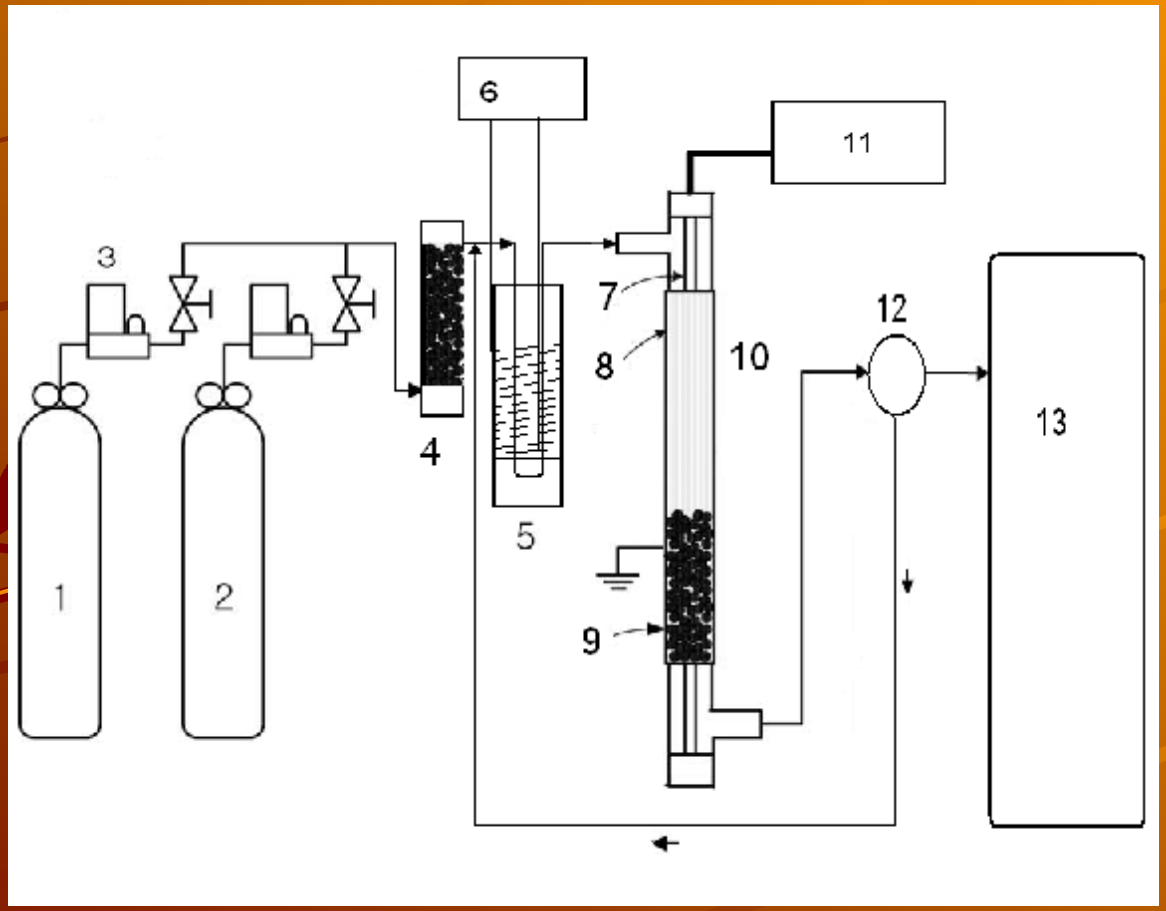
Materials and Methods

- New approach for ammonia production from renewable hydrogen and energy



Materials and Methods

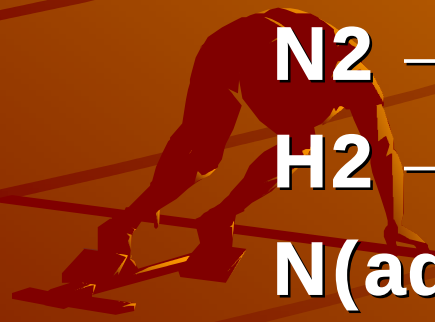
- Schematic diagram of the experimental apparatus



(1) nitrogen;
(2) hydrogen;
(3) mass flow controller;
(4) dryer;
(5) gas purification;
(6) temperature control instrument;
(7) inner electrode;
(8) outer electrode;
(9) catalyst bed;
(10) plasma reactor;
(11) power supply;
(12) compressor; and
(13) ammonia storage tanks.

Materials and Methods

- Non-Thermal Plasma Assisted NH_3 Synthesis



N2 → 2N(ad)

H2 → 2H(ad)

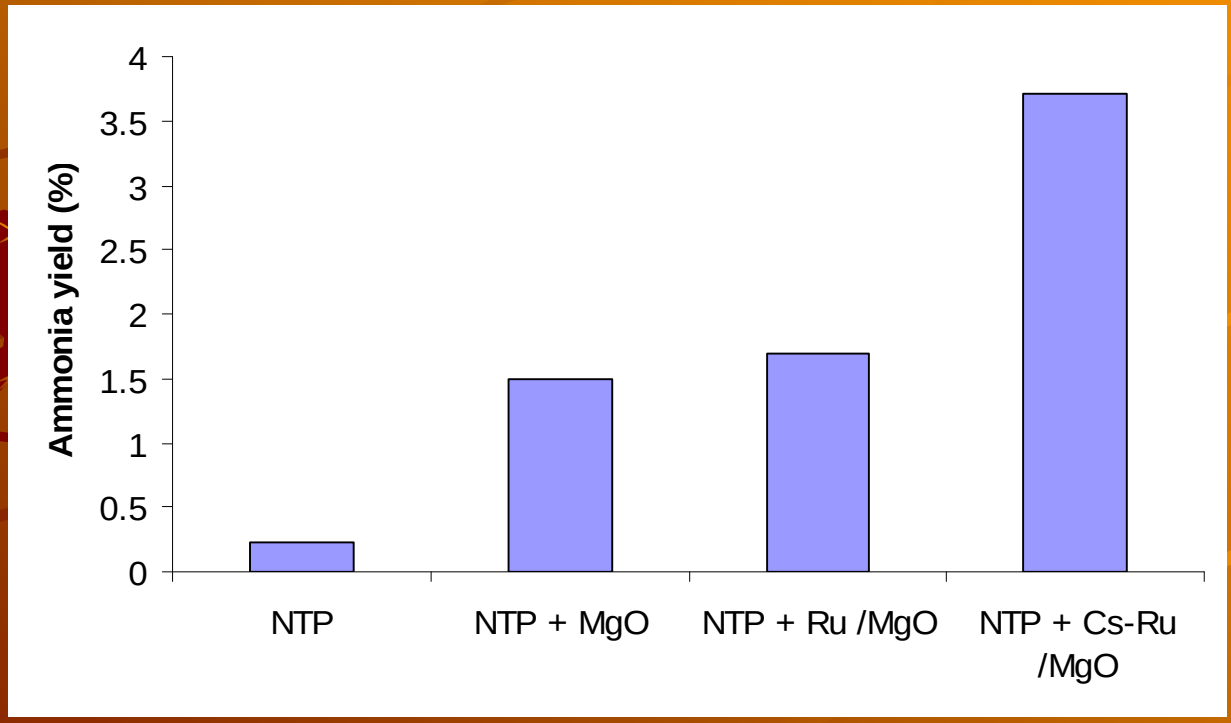
N(ad) + H(ad)→ NH(ad)

NH(ad) + H(ad) → NH2(ad)

NH2(ad) + H(ad) → NH3(ad)

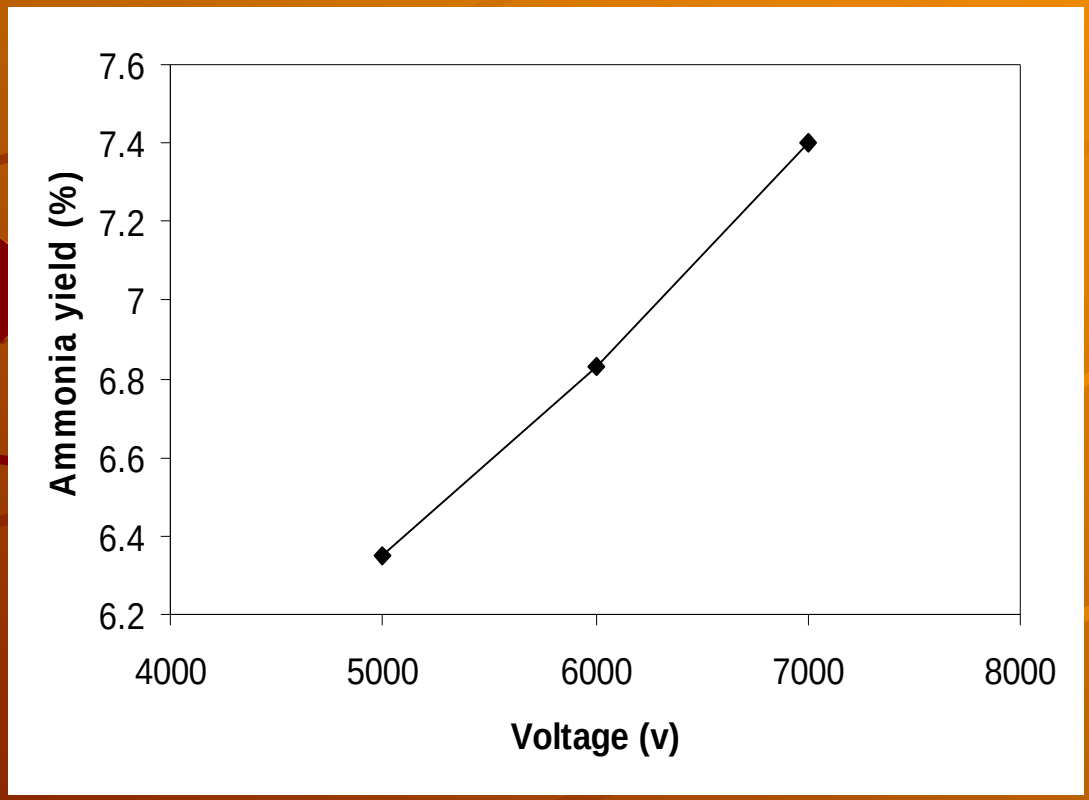
Results and Discussion

- Ammonia synthesis under different catalyst



Results and Discussion

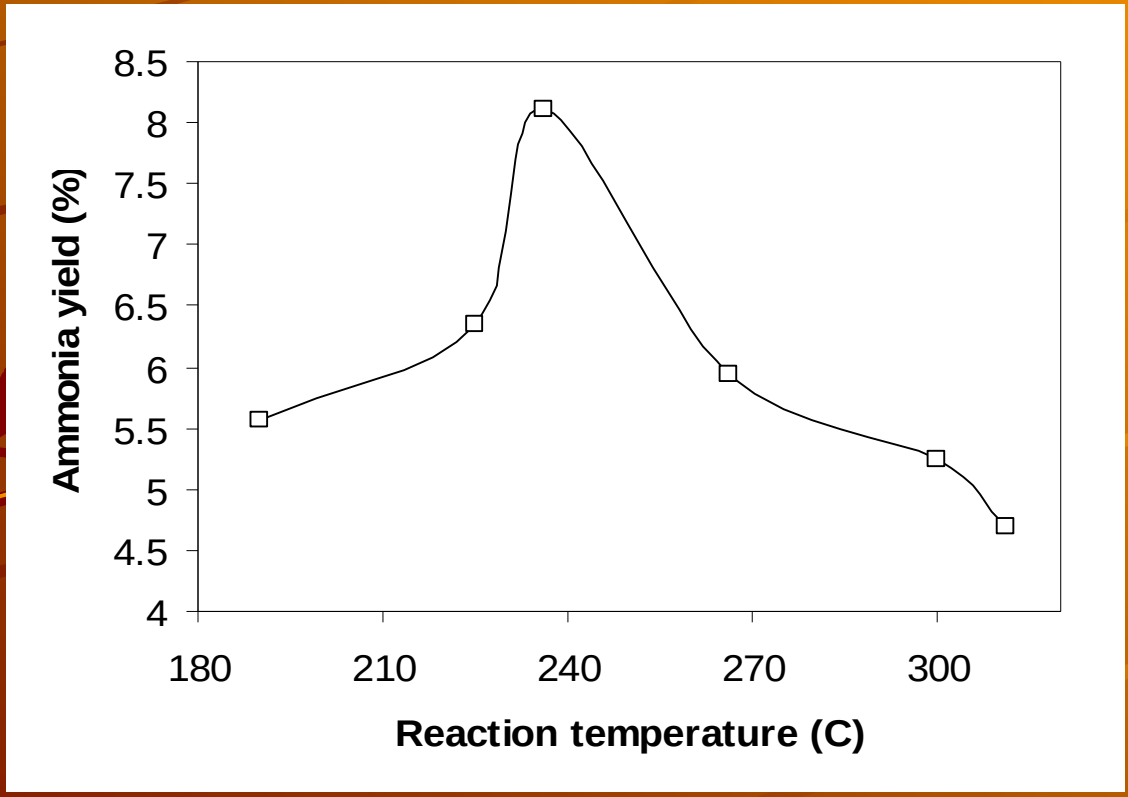
- Effect of applied voltage on ammonia formation



catalyst: Cs-Ru/MgO-TiO2; frequency: 8000Hz; N2 and H2 total flow rate: 60ml/min.

Results and Discussion

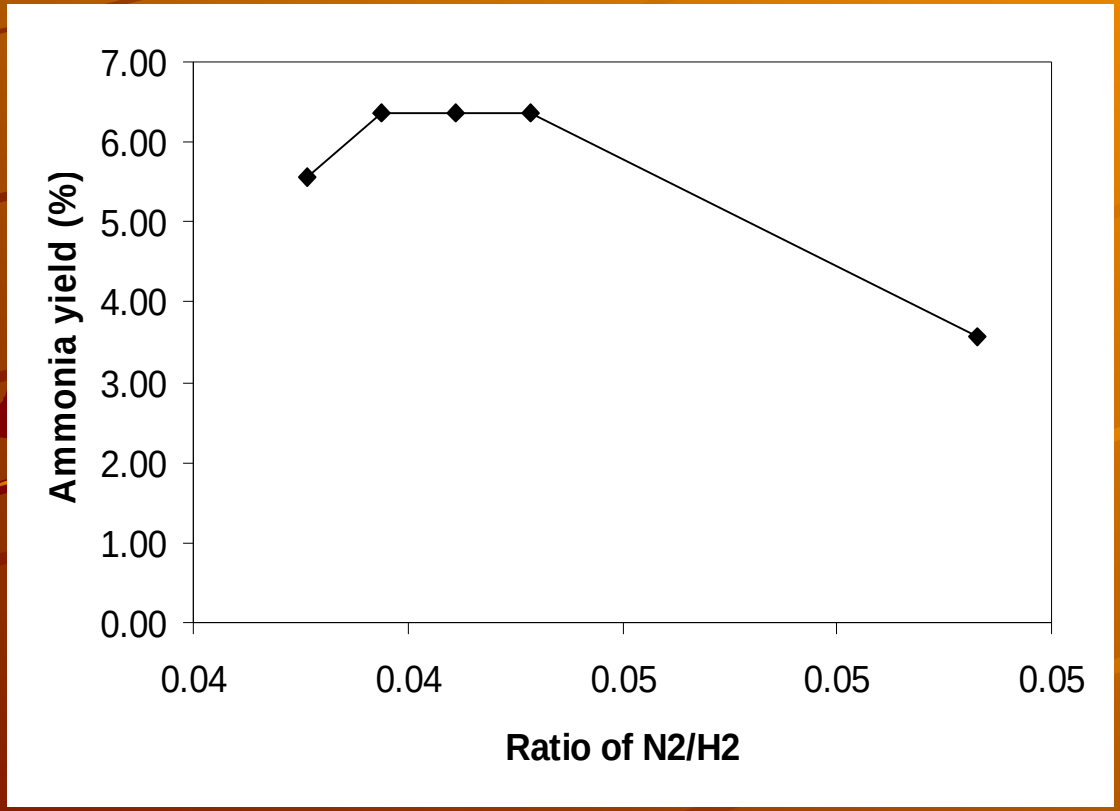
- Ammonia formation as a function of temperature



catalyst: Cs-Ru/MgO-TiO2; VN2:VH2=1:3, N2 and H2 total flow rate: 60ml/min, voltage: 5000V, frequency : 10000Hz.

Results and Discussion

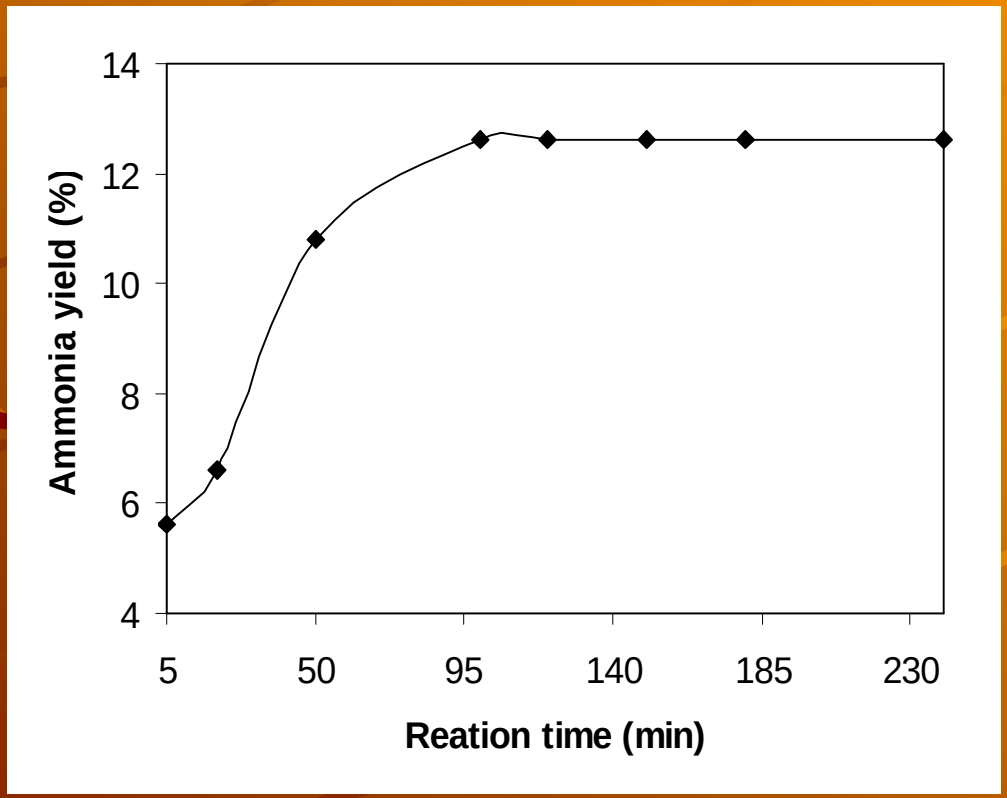
- Effect of ratio of N2/H2 on ammonia formation



catalyst: Cs-Ru /MgO-TiO2; voltage : 5000V, frequency: 10000Hz; N2 and H2 total flow rate: 60ml/min

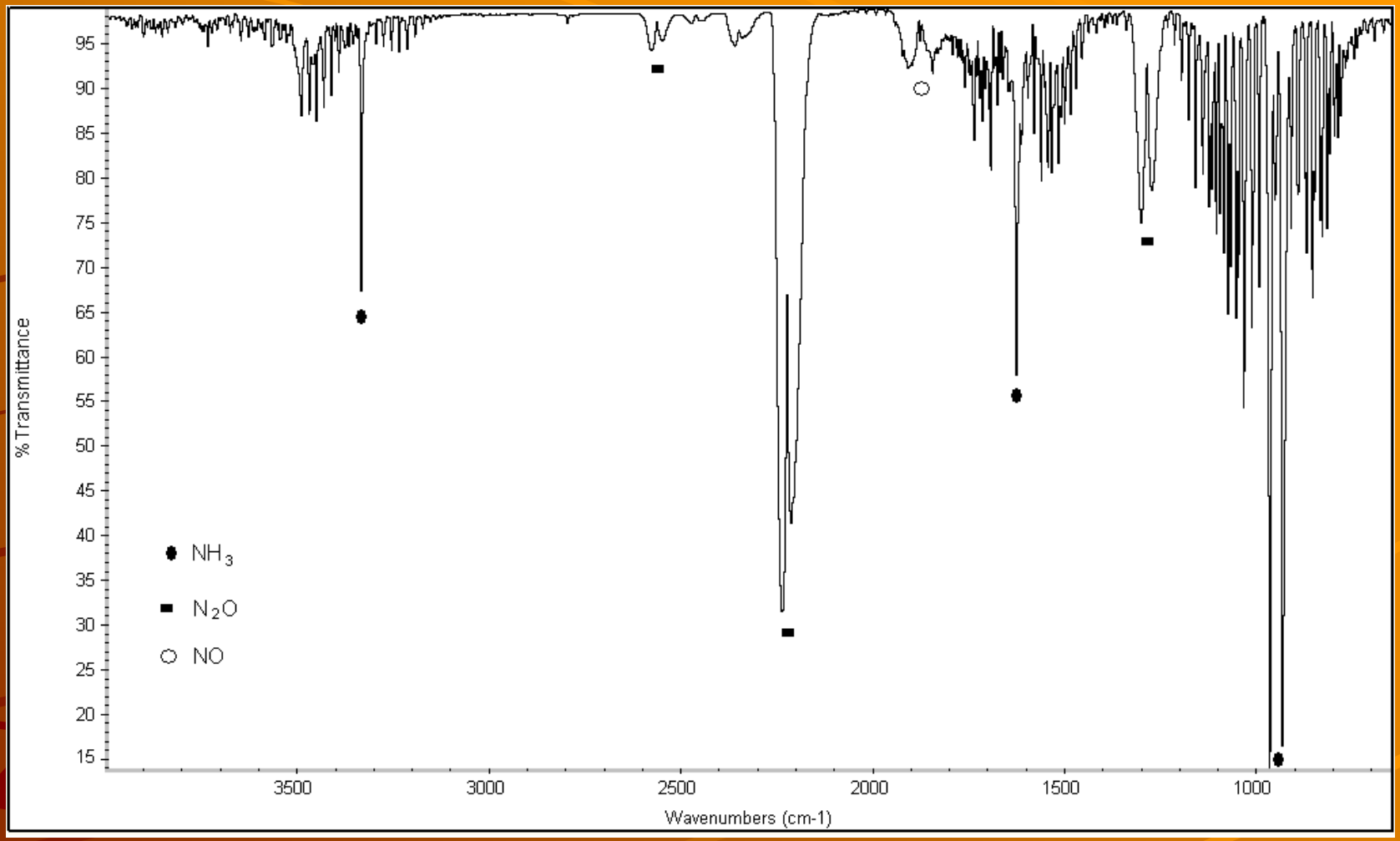
Results and Discussion

- Ammonia formation as a function of time in an NTP reactor with catalysts

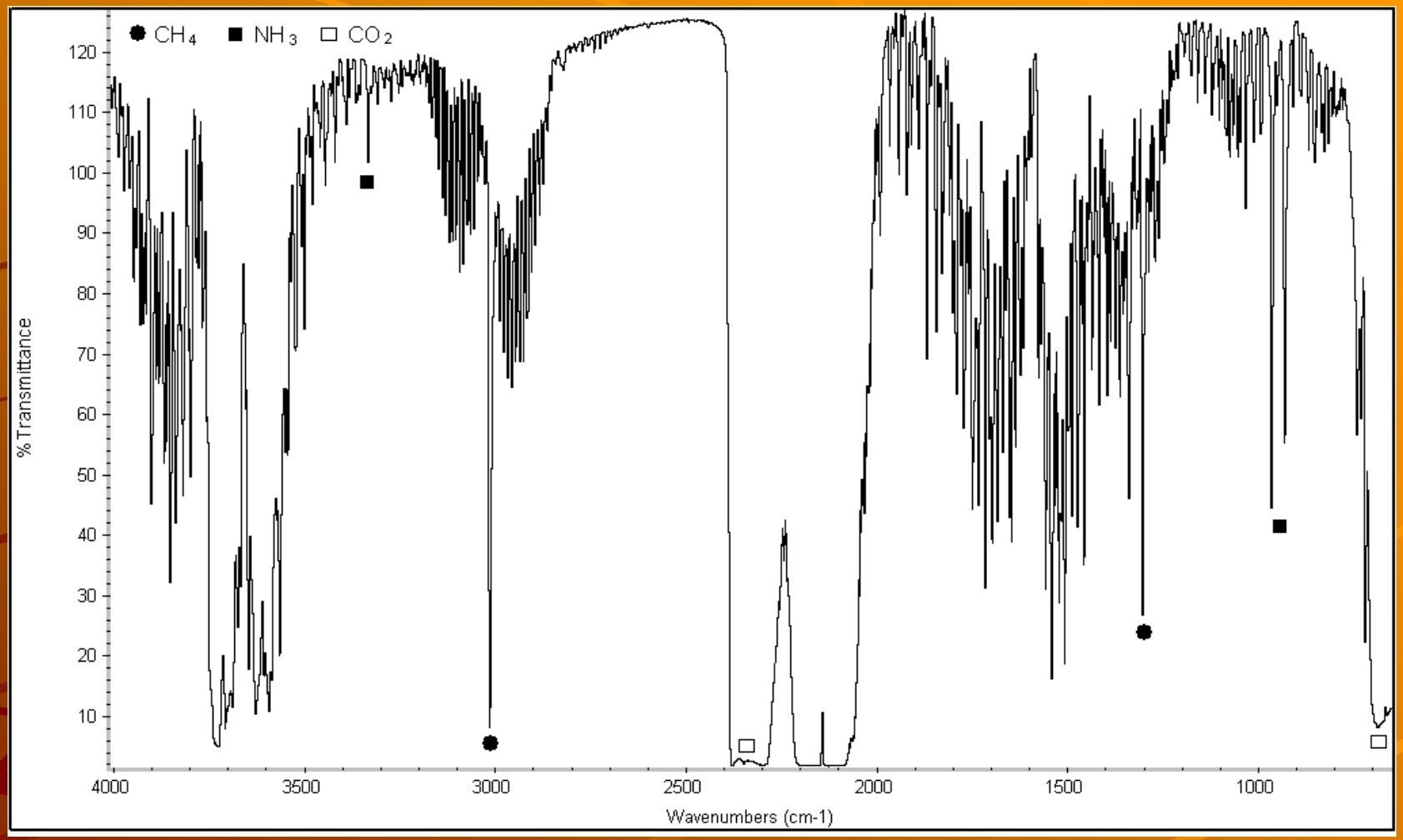


Comparison Between Traditional Thermochemistry and NTP Assisted Catalysis.

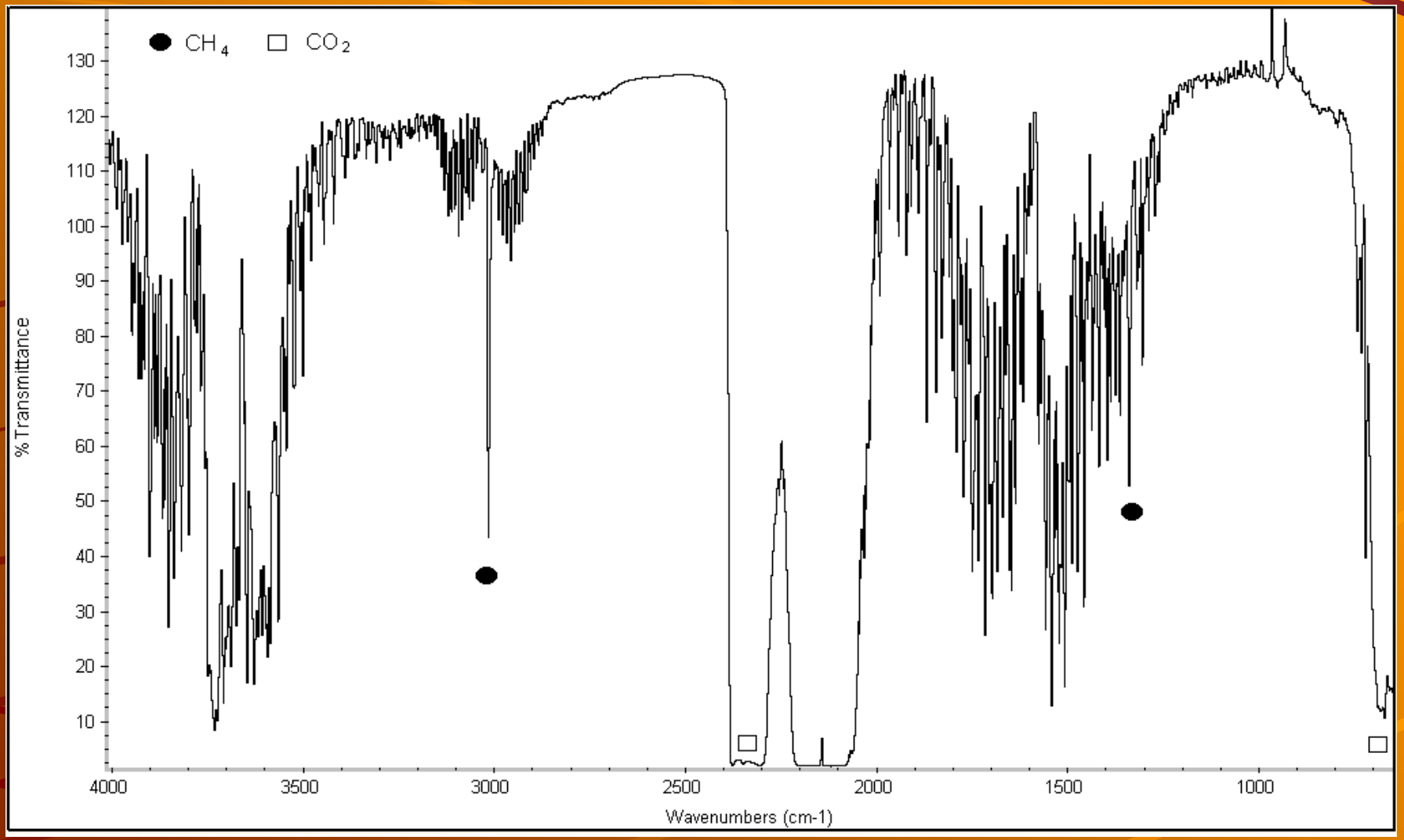
Reactants	Traditional high temperature and high pressure	Low temperature and atmospheric pressure	
		Without NTP	*With NTP*
(1) $N_2 + H_2$	NH_3	-	NH_3
(2) $N_2 + H_2O$	-	-	NH_3, N_2O
(3) $CO + N_2 + H_2O$	CO_2, H_2, NH_3	-	CH_4, NH_3, CO_2, N_2O, NO, ……
(4) $CO + H_2O$	CO_2, H_2	-	CH_4, CO_2, H_2



FT-IR spectrum of reaction of N2 and H2O on Ru-Pt-Cs/MgO catalyst

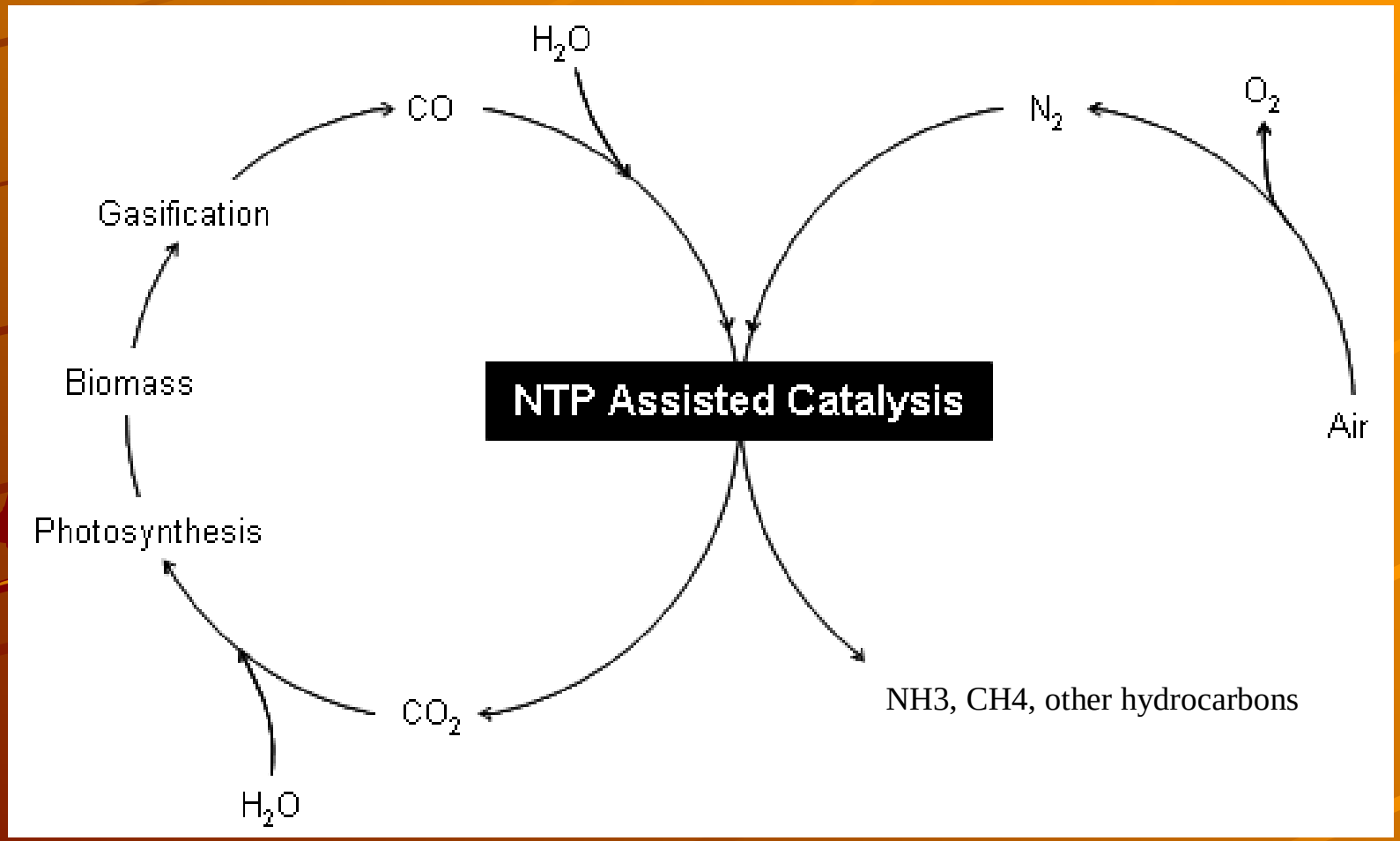


FT-IR spectrum of reaction of N2, CO, and H2O.



FT-IR spectrum of reaction of CO and H2O.

NTP Assisted Catalysis Reactions



Conclusions

- The non-thermal plasma generated by dielectric barrier discharge can ionize and dissociate N_2 and H_2 molecules to form a large number of activated species, which react to produce ammonia molecules.

Conclusions

- The concentration of ammonia produced depends on applied voltage, frequency, temperature, and the catalysts and promoters. The highest concentration reached 12.6% in this study.

Conclusions

- The Ru-based catalyst had high catalytic activity at low temperature. It also indicated that ammonia synthesis with non-thermal plasma and promoted catalyst was much less temperature dependent than with other catalytic processes.

Conclusions

- High reaction activities can be attained even when the feed gas composition varied to a large extent.
- Ammonia synthesis by non-thermal plasma with promoted catalysts should have a great potential to become an innovative commercial technology.

Thanks!

Questions?

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