CO_2 Conversion to Organic Compounds and Polymeric Precursors

Authors: Aurea A. Barbosa, Heitor B. Pereira Ferreira, Claudio J A Mota and
Jussara Lopes de Miranda*

Institute of Chemistry

Federal University of Rio de Janeiro (UFRJ)

Rio de Janeiro
Brazil

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Outline

- Energy Supply in Brazil
- Presentation of the Lacqua's projets
- Motivation for CO_2 conversion
- Industrial uses of CO_2
- Challenges for CO_2 conversion
- CO_2 Conversion by heterogeneous catalysis
- CO_2 Conversion by Homogenous catalysis
- CO_2 Capture using metal organic frameworks
- Future Goals

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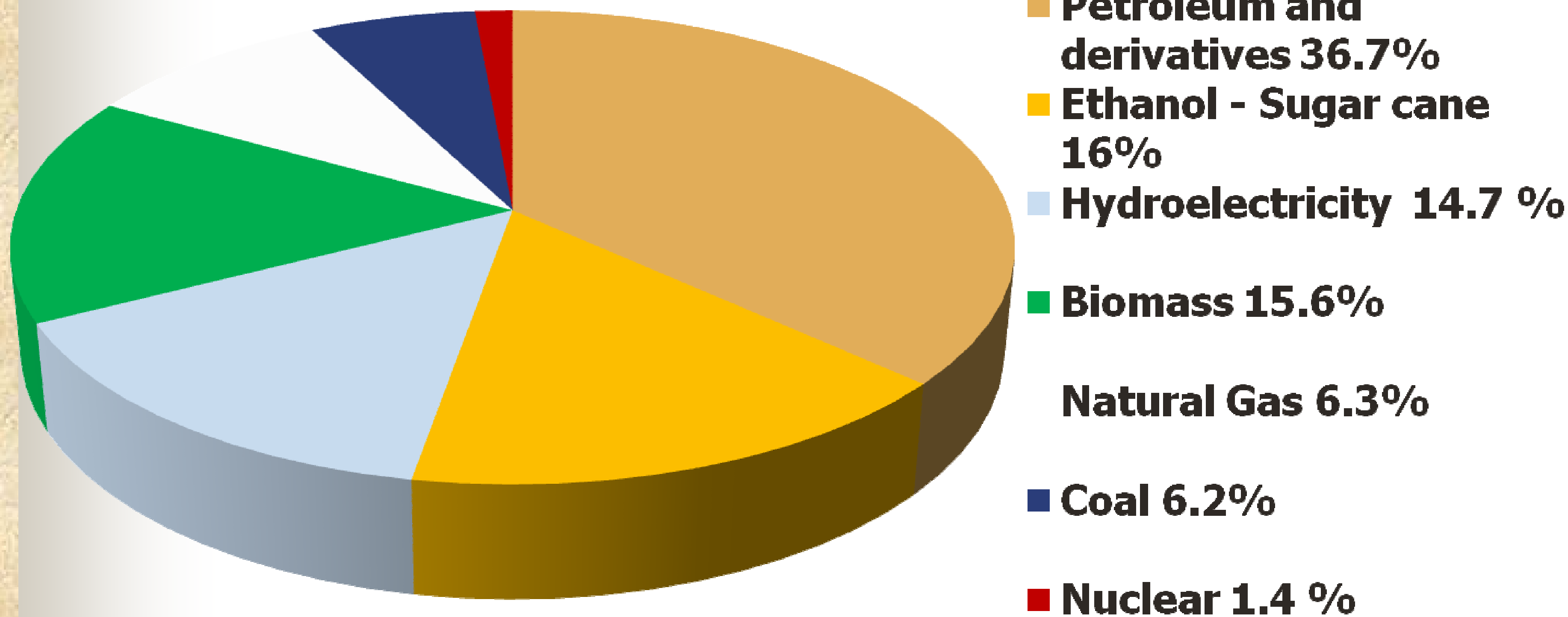
Energy Supply in Brazil

Energy Supply in Brazil , 2007
46.4 % of Renewable Energy



LACQUA –IQ/UFRJ

Laboratory of Catalysis and Environmental Chemistry

CO_2

CAPTURE

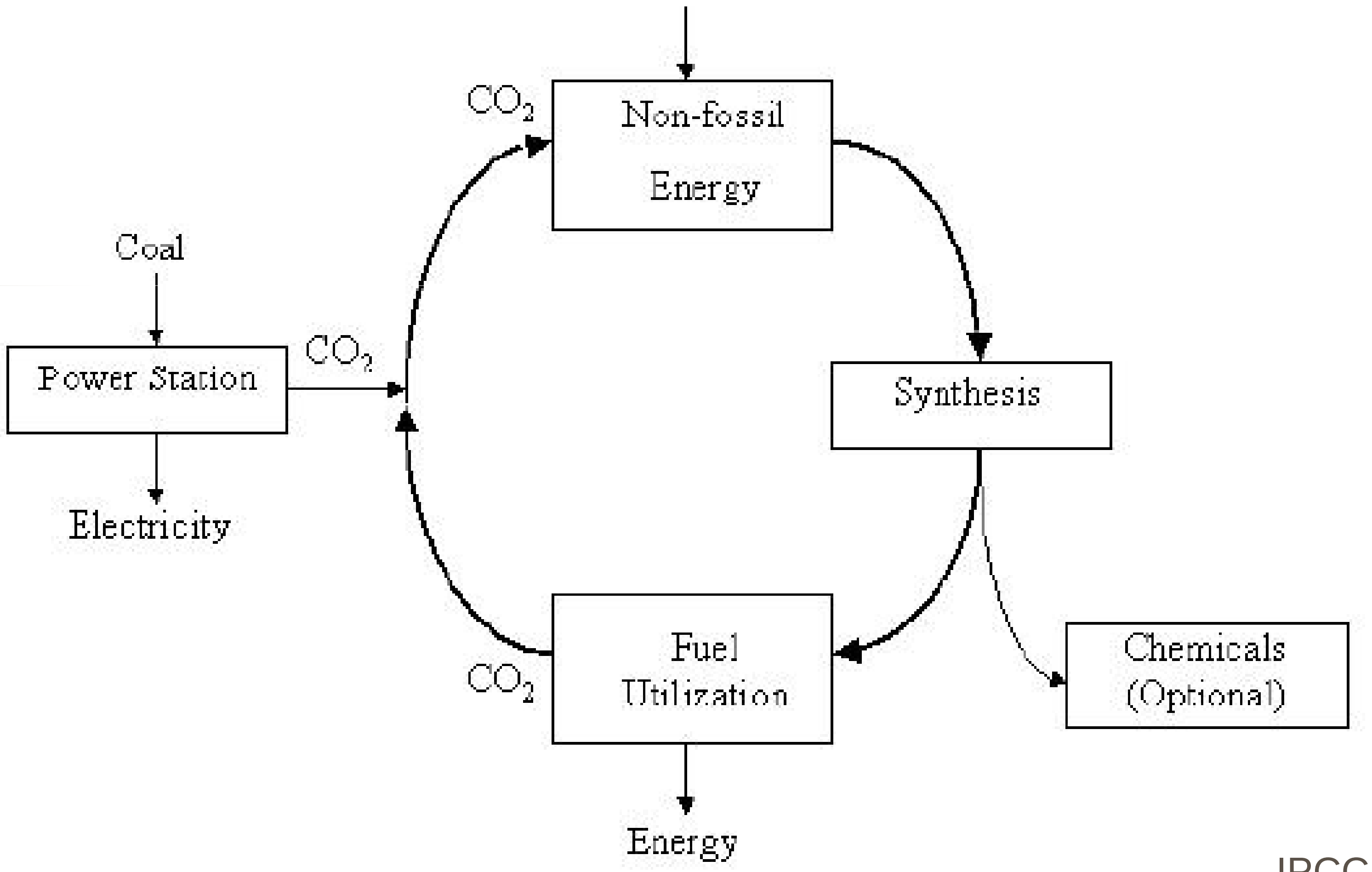
CO_2 Capture with MOFs
(Metal Organic Frameworks)

CONVERSION

Conversion of CO_2 into Organic Products

METHANOL, FORMIC ACID, FORMALDEHYDE
POLYMERS PRECURSORS

Motivation for CO_2 Conversion



A CO_2 based secondary energy cycle (Smith and Thambimuthu 1991)

IPCC reports

Main Sources of CO_2

Table SPM.1. Profile by process or industrial activity of worldwide large stationary CO_2 sources with emissions of more than 0.1 million tonnes of CO_2 ($MtCO_2$) per year.

Process	**Number of sources**	**Emissions ($MtCO_2$ yr^{-1})**
Fossil fuels		
Power	4,942	10,539
Cement production	1,175	932
Refineries	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas processing	Not available	50
Other sources	90	33
Biomass		
Bioethanol and bioenergy	303	91

IPCC - *Third Assessment Report (TAR)*

Current Industrial Uses of CO_2

Industrial Processes that use CO_2	Global Capacity /year	Quantitity of CO_2 fixed
Urea	95 Mt	54 Mt
Salicylic Acid	70 Mt	25 Mt
Methanol	20 Mt	2 Mt
Cyclic Carbonates	80 Mt	~ 40 kt
Polypropilenocarbonate	70 Mt	~30 kt

Aresta, M. , ***Carbon Dioxide Recovery and Utilization***, Kluwer Academic Publishers, Netherlands, 2003

Expected Benefits from CO_2 Conversion

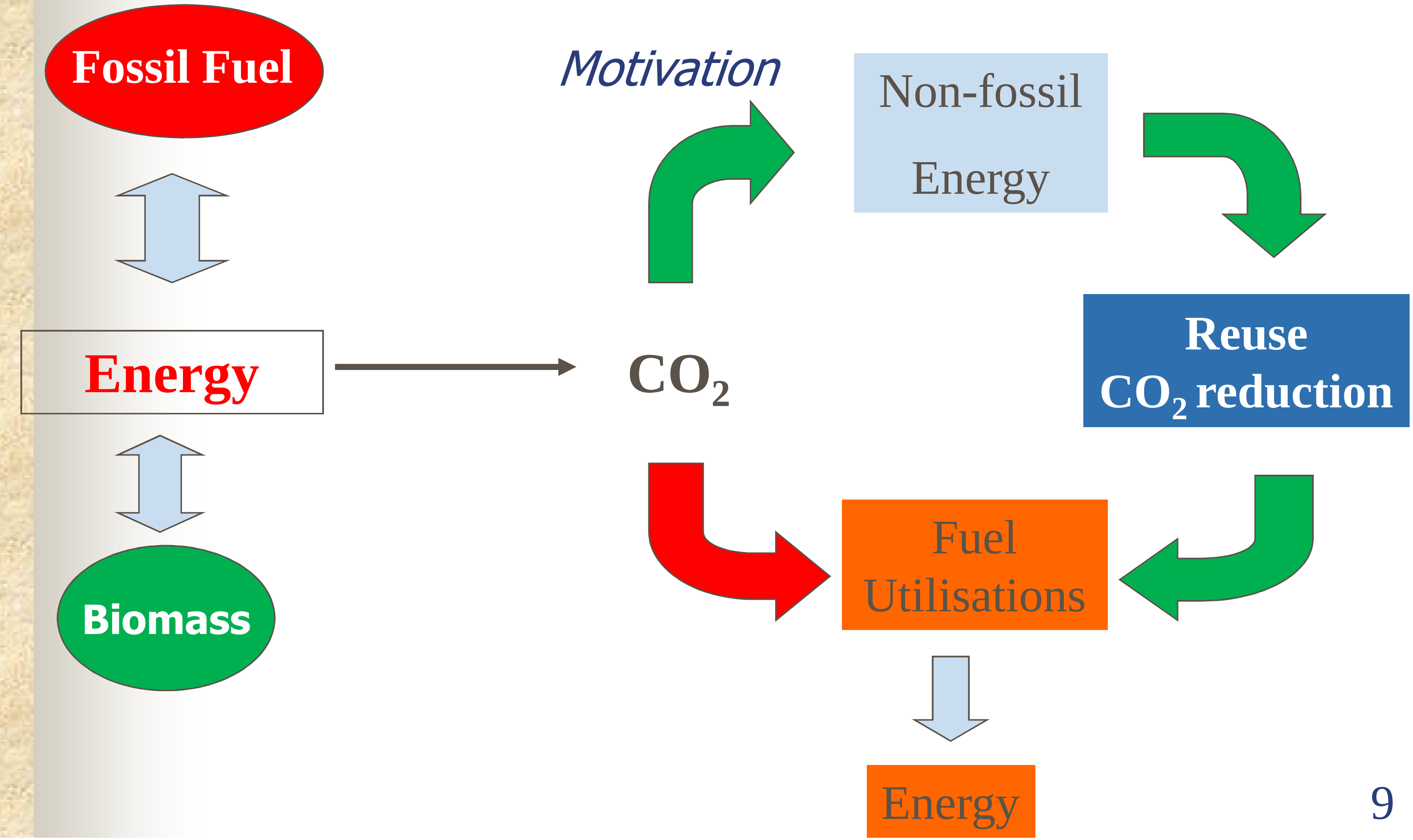
Environmental → Contribution to the reduction in CO_2 emissions

Economical → CO_2 conversion into products of economical value

Social → Contribution to a better human health & better climate conditions

Scientifical → Synthesis of new designed catalysts and the study of C1 chemistry

Conversion of CO_2 into Organic Products



Challenges to CO_2 Conversion

- Use of CO_2 as the starting material for the synthesis of organic chemical products, carbohydrates and polymers

- Need of pure and concentrated CO_2 for conversion processes – implies the costs of capture and transportation

-Energy demand for CO_2 conversion – use of energetic reagents and good catalysts

- Global market context for the products that are synthesized from CO_2

Examples of Industrial Processes That Use CO_2

Urea Production

$$CO_2 + 2\ NH_3 \longrightarrow H_2N\text{-}CO\text{-}NH_2 + H_2O$$

T= 185-190°C, P=150-220 atm

It occurs in two steps

$$CO_2 + 2\ NH_3 \longrightarrow H_2N\text{-}COO^{-}NH_4^{+}$$

$$H_2N\text{-}COO^{-}NH_4^{+} \longrightarrow H_2NCONH_2 + H_2O$$

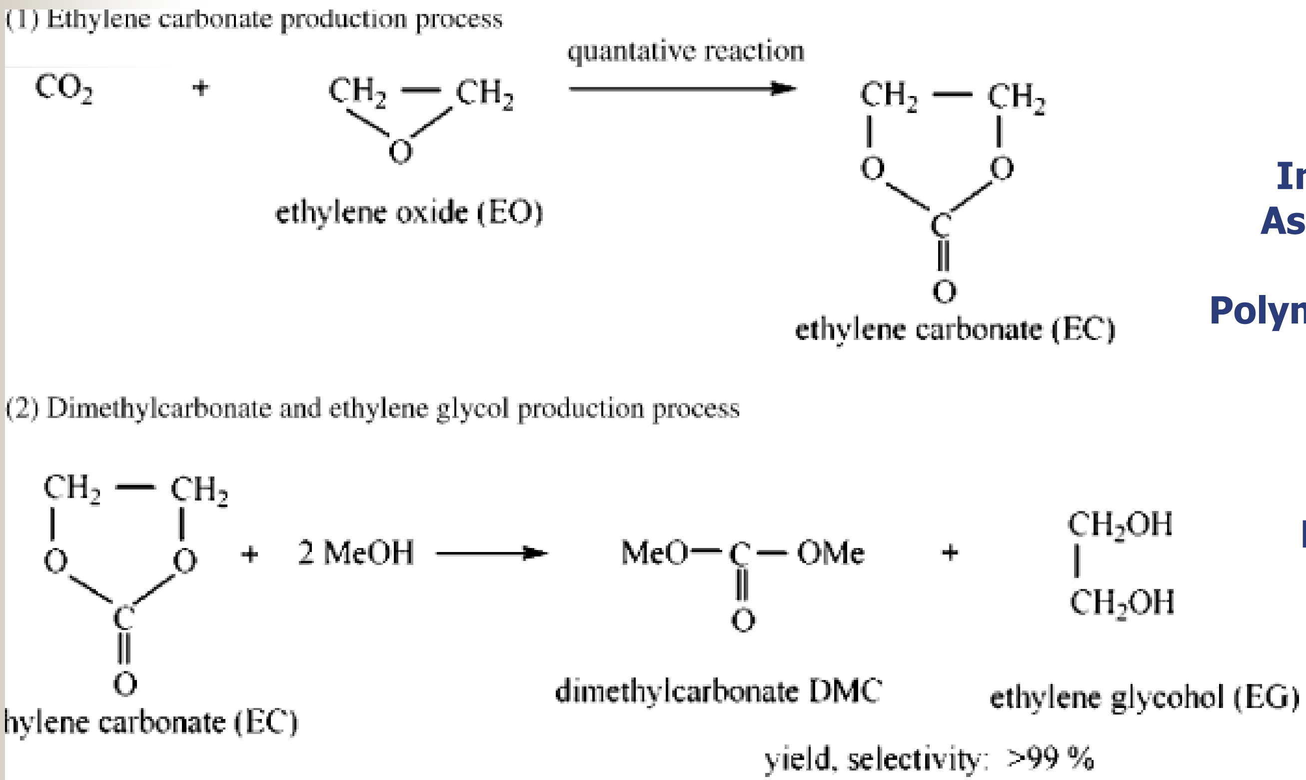
- It is the product that uses the greatest amount of CO_2
- Global production in 2002 – 100 millions of tons/year = 22 millions of tons CO_2
- More than 54 % of global capacity is in Southeast Asia
- Urea can be used as a fertilizer 46%) or raw material for carbonates
- It can be associated with CO_2 Capture

Production of Dimethyl Carbonate (DMC) without phosgene and chlorine

- The usual route for DMC synthesis

$$CO + Cl_2 \longrightarrow COCl_2$$

$$COCl_2 + 2\ CH_3OH \longrightarrow CH_3OCOOCH_3 + 2\ HCl$$



Industrial Process from Asahi Chemical Industry:

Polymers synthesis since 2002

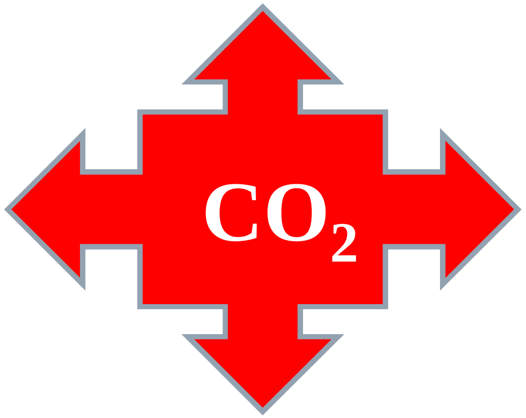
Production 50.000 ton/year

Removal of CO_2 1730 ton/10.000 ton PC

Some Features of CO_2 Conversion In Research

Methanol

Formic Acid, Formiates and amides



Dimethylcarbonate e polycarbonates

Petrochemicals

Metal catalysts : Ru, Rh, Ni, Pd, Pt
Homogenous and Heterogenous Catalysis.

Capture and Conversion of CO_2 into Organic Carbon Products and Polymeric Precursors

Synthesis of catalysts able to aid CO_2 conversion
Conversion of CO_2 into organic products

CO_2

CONVERSION

Fixation of CO_2 into Organic Products

METHANOL, FORMIC ACID, FORMALDEHYDE
PRECURSORS OF POLYMERS

EXPERIMENTAL

1- Heterogenous Catalysis- Hydrogenation of CO_2

Ni, Ru catalysts

$CO_2 + H_2 \longrightarrow$ Organic products

2- Homogeneous Catalysis – CO_2 reaction with methanol

Sn catalysts

$CO_2 + H_3C\text{-}OH \longrightarrow$ Organic products

Experimental Steps: Part I - **Heterogenous Catalysis- Hydrogenation of CO_2** - Synthesis of Catalysts

- *Synthesis of catalysts based on complexes of nickel and ruthenium – eleven catalysts were synthesized.*
- *Synthesis of the mesoporous (silicate)*
- *Intercalation of the cationic complexes of nickel and ruthenium into the mesoporous*
- *Characterization of the catalysts:*

- Elemental Analysis

- Infrared Spectroscopy

- X-ray diffraction

- Nuclear Magnetic Resonance

- Thermogravimetric Analysis

- Electronic analysis

Intercalation results

Sample	Distance d (Å)	Δ d (Å)
Sodium mesoporous	15.21	-
mesoporous+surfactant /ButOH	20.67	5.46
Ni^{2+} intercalated	15.17	5.50
Ru^{3+} intercalated	15.28	5.39
Cat Ni1 intercalated	18.21	2.46
Cat Ni2 intercalated	18.92	1.75
Cat Ru1 intercalated	18.21	2.46

Conversion Results of Heterogeneous Catalysis

11 Catalysts synthesized – 7 were active – 20 to 30 % of conversion, pressure = 1 atm

Catalyst	Product	Temp (°C)
Cat 1	Formaldehyde	149
Cat 2	Formaldehyde	111-124
Cat 3	Methanol, Formic acid, formaldehyde	150-152
Cat 4	Methanol	152
Cat 5	Formic acid	152
Cat 6	Methanol	150-152

Conclusions from Conversion of CO_2 into Organic Products by Heterogeneous Catalysis

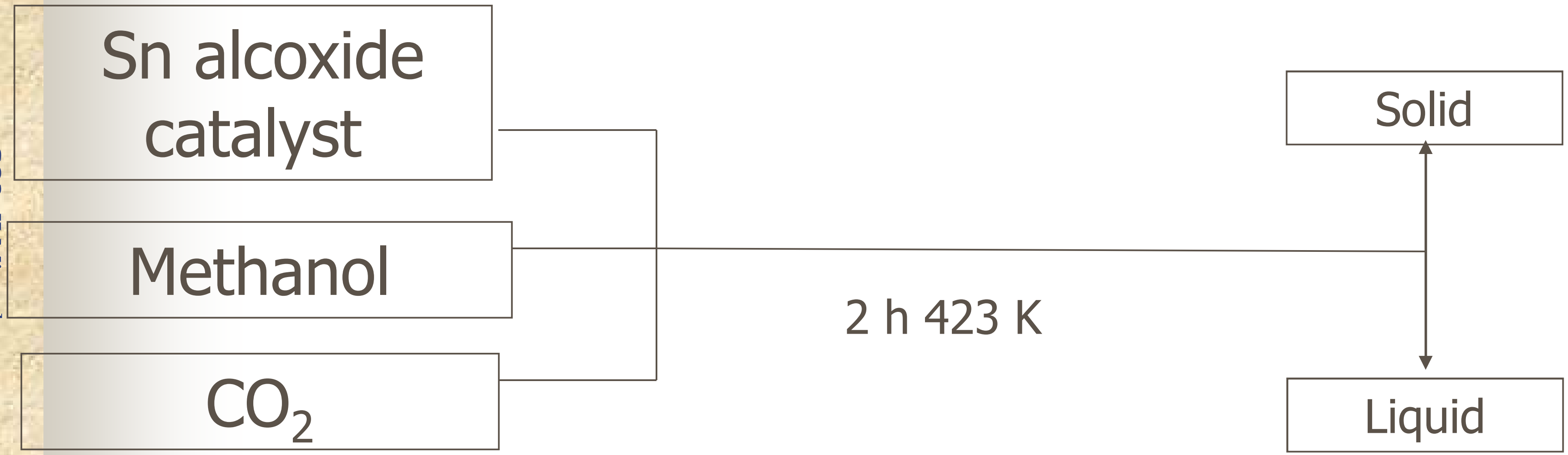
- *11 Catalysts were synthesized and characterized*
- *Seven catalysts were able to convert CO_2 → 30 % of total conversion*
- *The main products of the conversion were: methanol, formic ac. and formaldehyde*
- *Mild conditions for conversion : P= 1 atm and ΔT = 120 to 150 °C*
- *1 Patent submitted.*

2- CO_2 Conversion by Homogeneous Catalysis
CO_2 reaction with methanol

Sn modified alcoxide catalyst

CO_2 + H_3C-OH → Organic products

catalytic test in a Parr reactor



GCMS Analysis

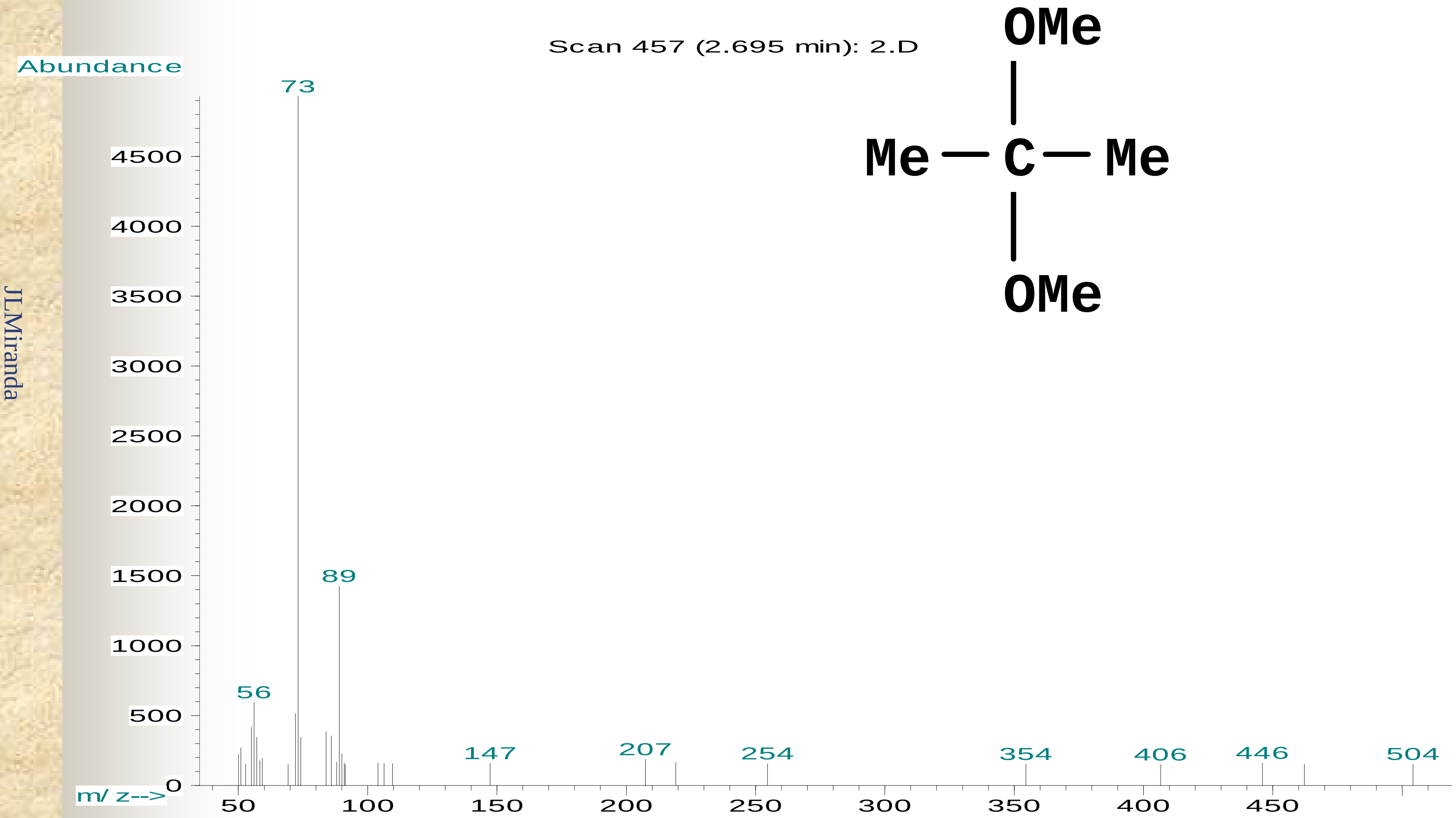
The Sn catalyst before and after the Conversion Test

Data from near infrared spectrum and far infrared spectrum of the catalyst before and after the catalytic test showed that

↓

The catalyst is stable

GCMS Spectrum of the obtained product



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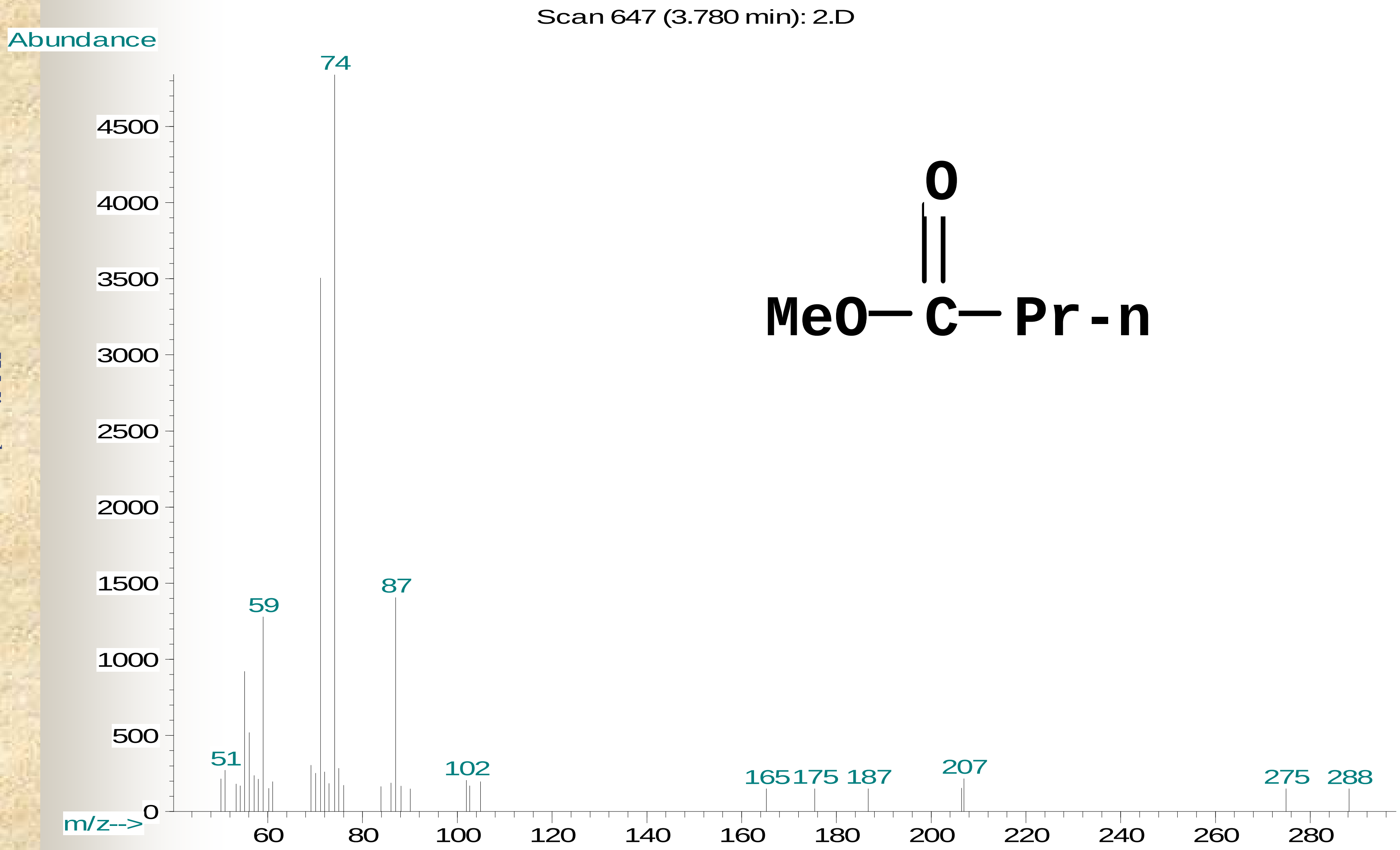
GCMS Spectrum of the obtained product



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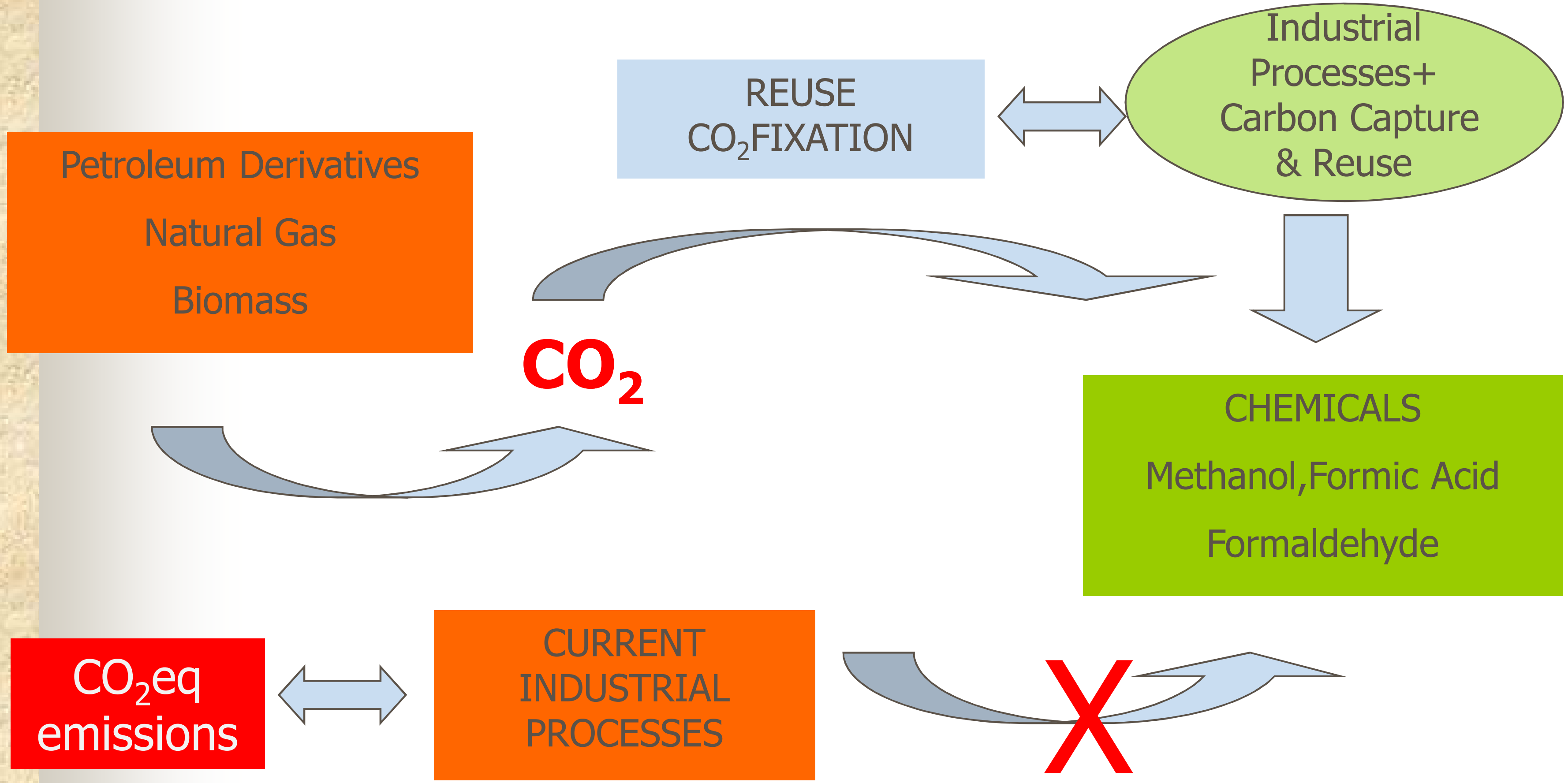
Conclusions from Homogeneous Catalysis
Conversion of CO_2 into Organic Products

-CO_2 insertion into Sn-O bond of the catalyst
- Formation of Oxygenated organic products

Conversion of CO_2 into Organic Products



Projects on CO_2 Capture

-Synthesis of new metal organic frameworks : chromium, copper and zirconium

- Synthesis of MOFs with lower cost

- Collaboration with Professor Christian Serre- Institute Lavoisier, Université de Versaillles Saint-Quentintin-En-Yvelines.

Future Goals

- Study of the recycle of the catalysts

- Comparison between nickel and ruthenium catalysts

- Use of zinc catalysts in homogeneous catalysis

- Synthesis of new MOFs with lower cost and greater selectiveness

- Use of ethanol to react with CO_2

Acknowledgments

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LACQUA´ S TEAM

Prof Jussara L Miranda – IQ/UFRJ

Prof Luiza C Moura- IQ/UFRJ

Prof Marco Barreto – IQ/UFRJ

Marcio G. Franco (Msc)

Áurea A. Barbosa (phD)

Heitor Breno Ferreira (phD)

Elisângela Souza (Msc)

Sueli Akemi (Msc)

Francisca Sobral (Msc)

Fernanda Luna da Silva (Grad.)

Lorraine Greco (Grad.)

Collaborations

Chirstian Serre- Université Yves-Saint-Quentin- France

Prof. Claudio Mota – IQ/UFRJ - Brazil

Prof. Heloise Pastore- Unicamp – Brazil

Prof. Diana Azevedo- UFC- Brazil

Thank you for your attention

jussara@iq.ufrj.br

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