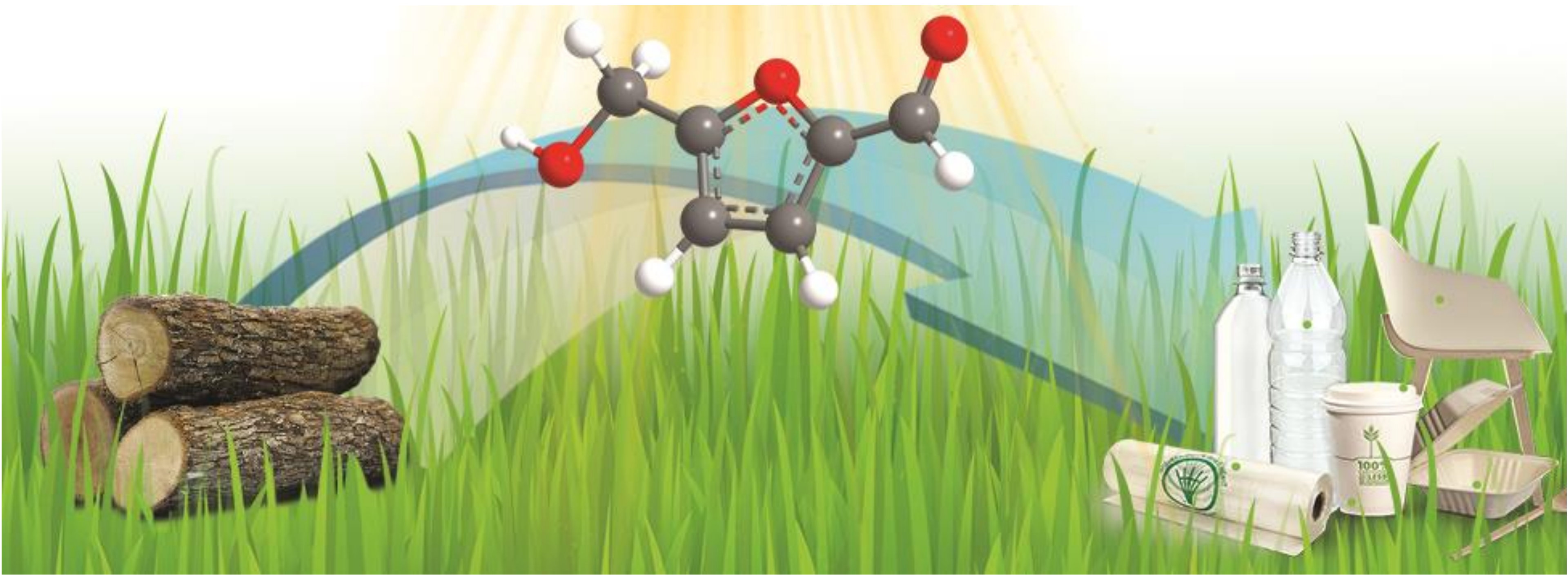
Niobium-based Solid Catalysts for Smart Biomass Conversion



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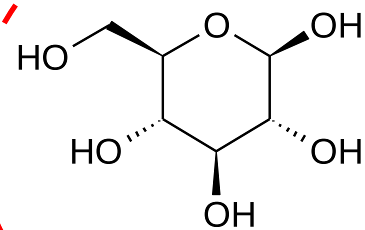
HOKKAIDO UNIVERSITY

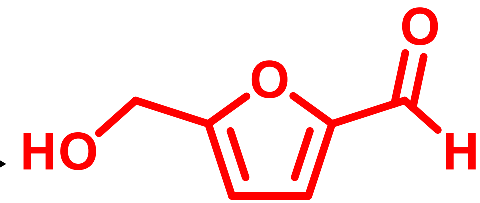
Biomass conversion for essential polymers

Cellulosic biomass

Hydrolysis

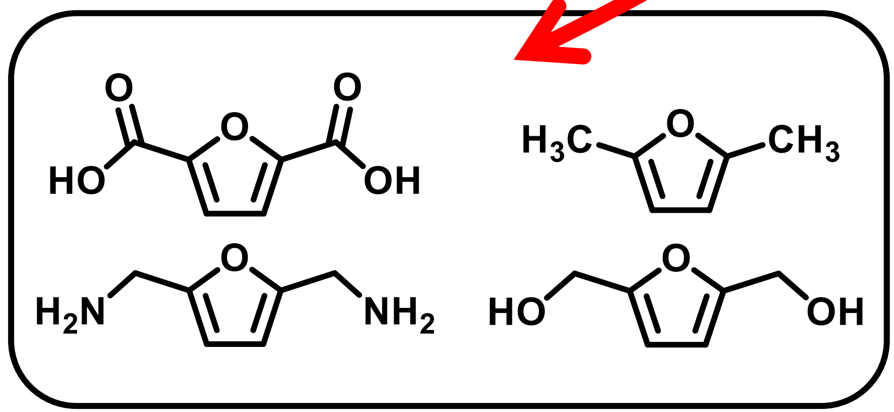


D-glucose



HMF

(5-hydroxymethyl)furfural

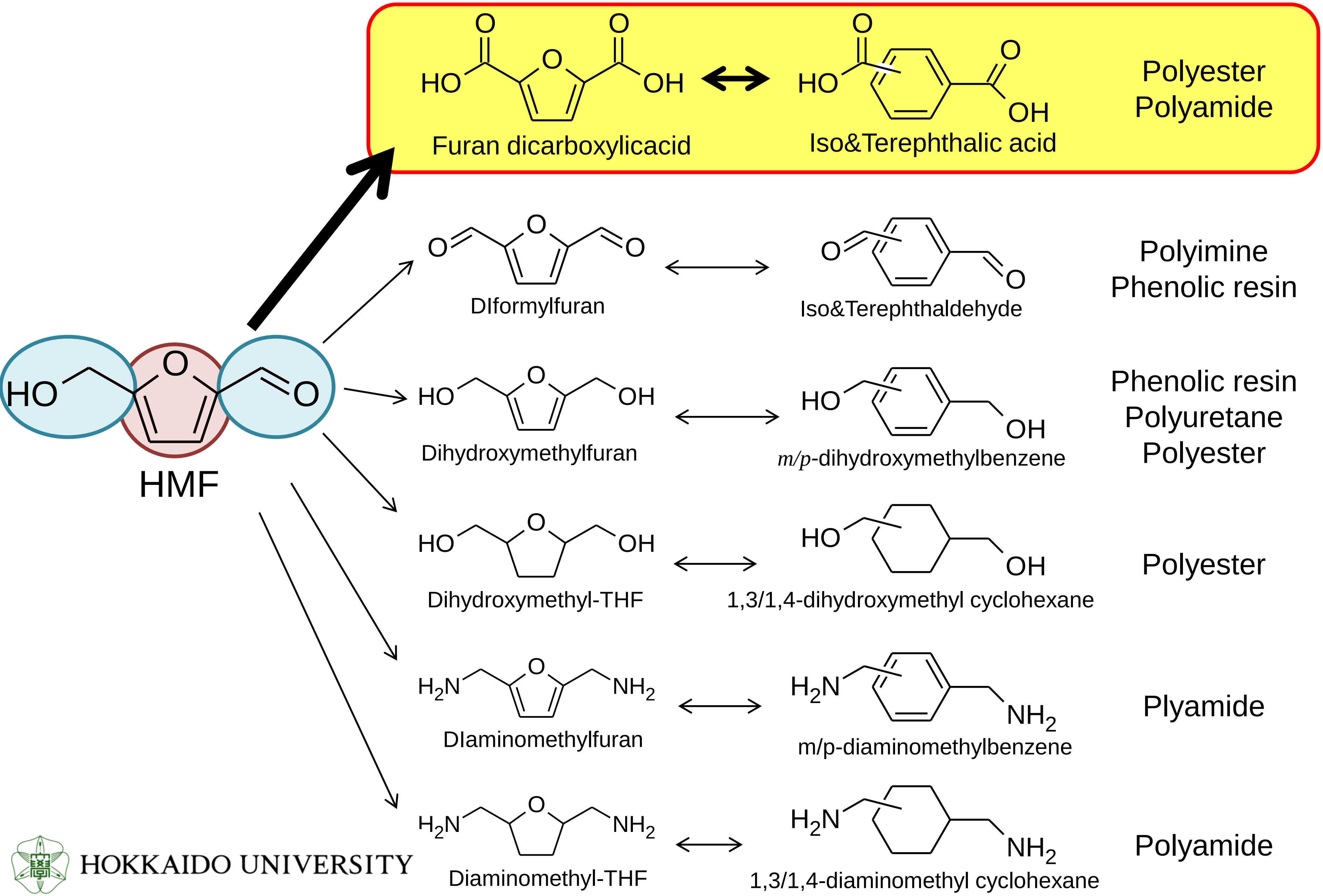


Platform molecules

Biobased polymers

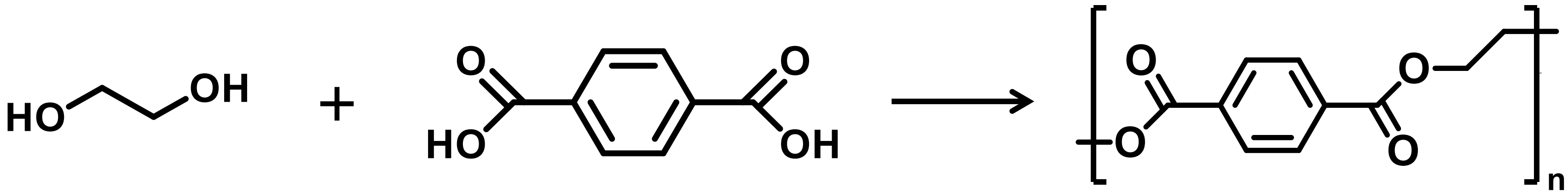
Polyester, Polyamide,
Polyuretane, etc…

Essential polymers synthesized from HMF



Polyalkylene furanate: a new class of biobased aromatic polyester

Fossil fuel-based terephthalate resin

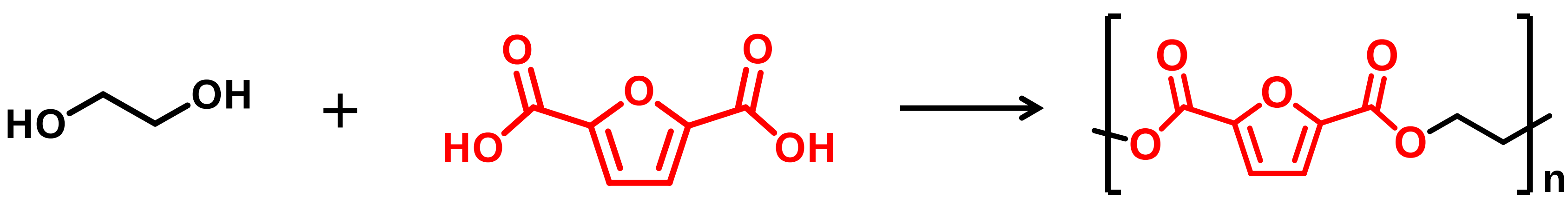


Ethylene glycol
(Appropriate diols)

Terephthalic acid
(TPA)

Polyethylene terephthalate
(PET: beverage bottle application)

Biobased furanoate resin

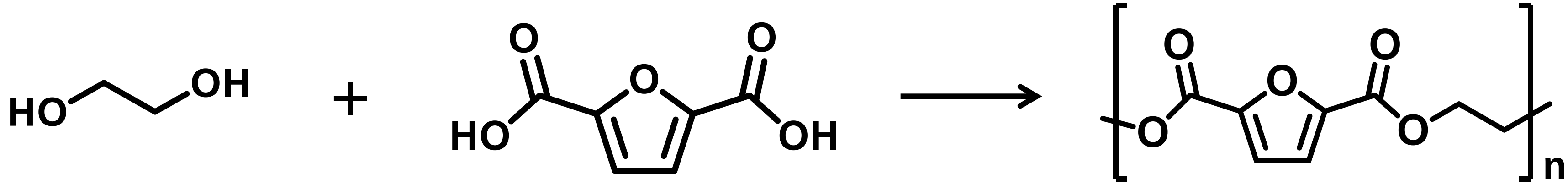


Ethylene glycol
(Appropriate diols)

Furan dicarboxylic acid
(FDCA)

Polyethylene furanate
(Polyalkylene furanoate)

Polyalkylene furanate: a new class of biobased aromatic polyester



Ethylene glycol
(Appropriate diols)

Furan dicarboxylic acid
(FDCA)

Polyethylene furanate
(Polyalkylene furanoate)

Biomass-based PEF vs petroleum-based PET

(1) Several excellent properties

- Gas barrier to O_2 (10 times), CO_2 (4 times), H_2O (twice)
- Tensile strength: 1.6 times
- Excellent thermal properties: High Tg (86 ºC) and low Tm (235 ºC)

(2) Application: beverage bottle, film, carpet, etc…

(3) Total amount of terephthalic acid consumed for PET and PBT production is 14.4 Mt in a year (Annual growth rate: 6.9%) → Reduction of CO_2 emission

Polyethylene furanoate (PEF) production in EU

PEFerence

The PEFerence project has received funding (3.7 billion euro) from the Bio-based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme (grant agreement No 744409).

BIO-BASED INDUSTRIES Public-Private Partnership

Bio-based Industries Consortium

Horizon 2020
European Union Funding
for Research & Innovation

SYNVINA functional. sustainable. bioplastics. | avantium | BASF We create chemistry | Tereos Looking forward, keeping close | //polytype OMV | LEGO

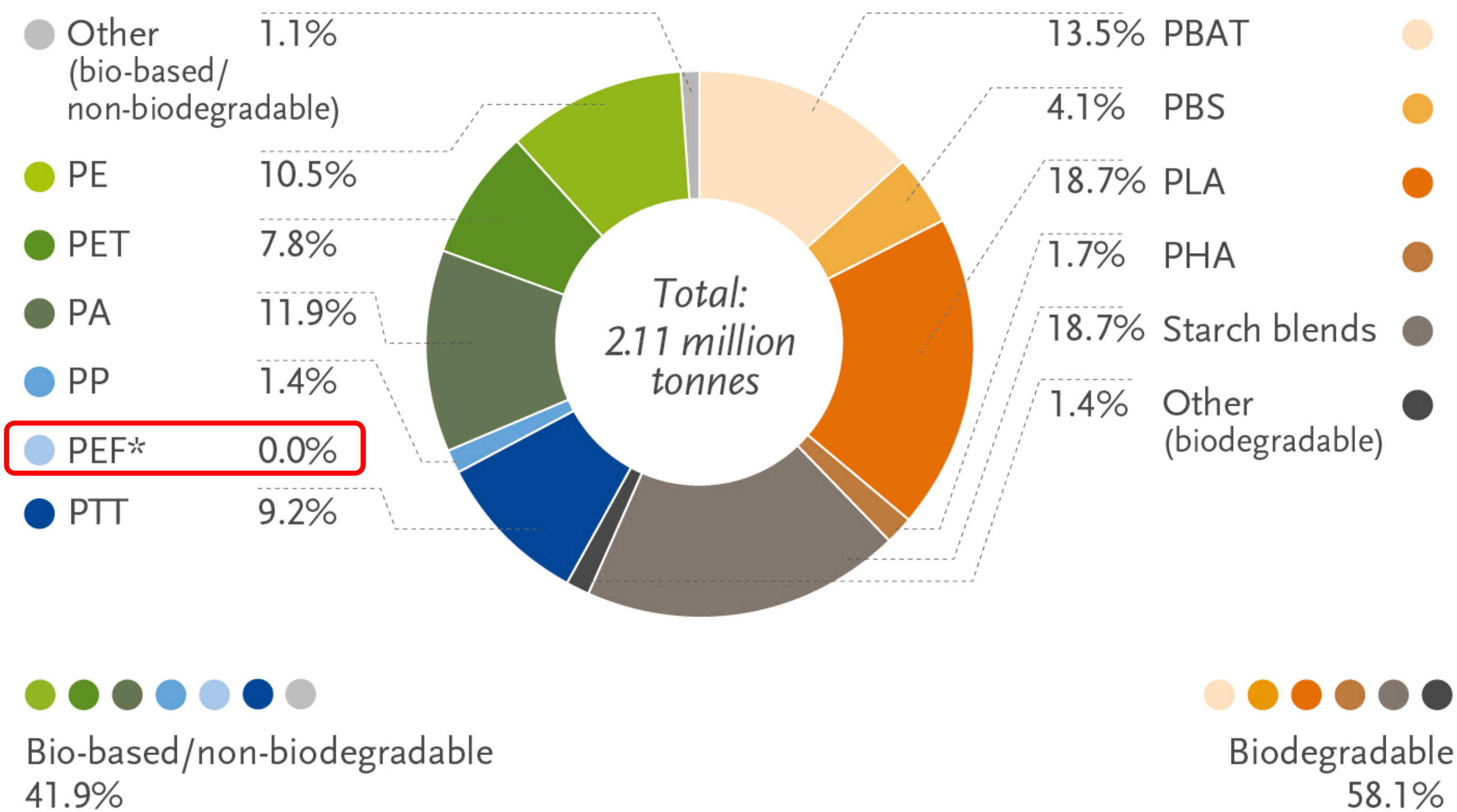
CRODA | Nestlé Research | ALPLA | SPINVERSE | nova Institut für Ökologie und Innovation

Objectives

- Engineer and build ***the flagship plant for the production of purified FDCA (50,000 tonnes/year)***
- Demonstrate and validate at least three 100% bio-based materials in end user applications
- Commercialize the 100% bio-based end products demonstrated in the project
- Demonstrate and optimize the new local biobased value chain from raw material sourcing to PEF end products
- Evaluate the environmental and socio-economic performance of the developed products

Polyethylene furanoate (PEF) production in EU

Global production capacities of bioplastics 2020 (by material type)

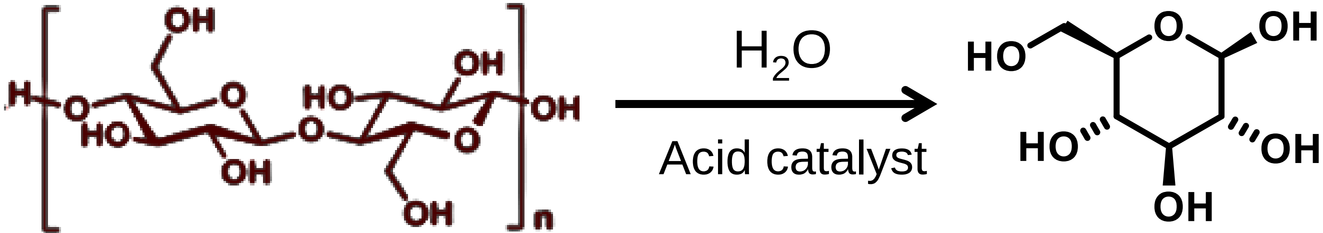


*PEF is currently in development and predicted to be available in commercial scale in 2023.

Source: European Bioplastics, nova-Institute (2020)
More information: ***www.european-bioplastics.org/market*** *and* ***www.bio-based.eu/markets***

PEF monomer production from lignocellulosic biomass

First step: **acid-catalyzed hydrolysis** of cellulose to glucose

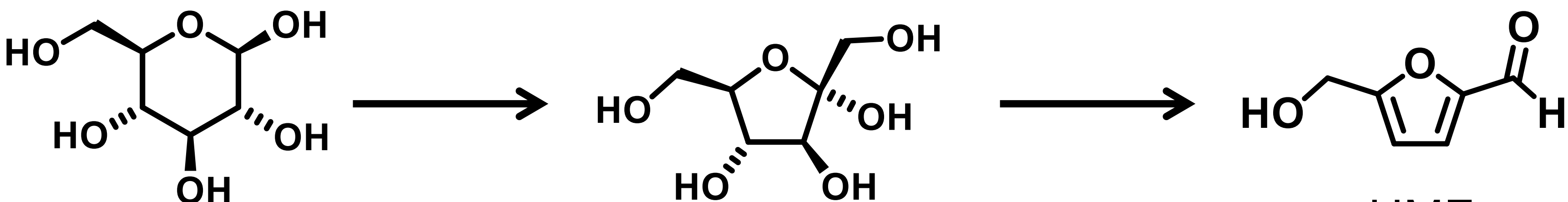


Cellulose

Glucose

Niobium technology (Niobic acid)

Second step: **acid-catalyzed dehydration** of glucose to HMF



Glucose

Fructose

HMF

Third step: aerobic oxidation of HMF to FDCA

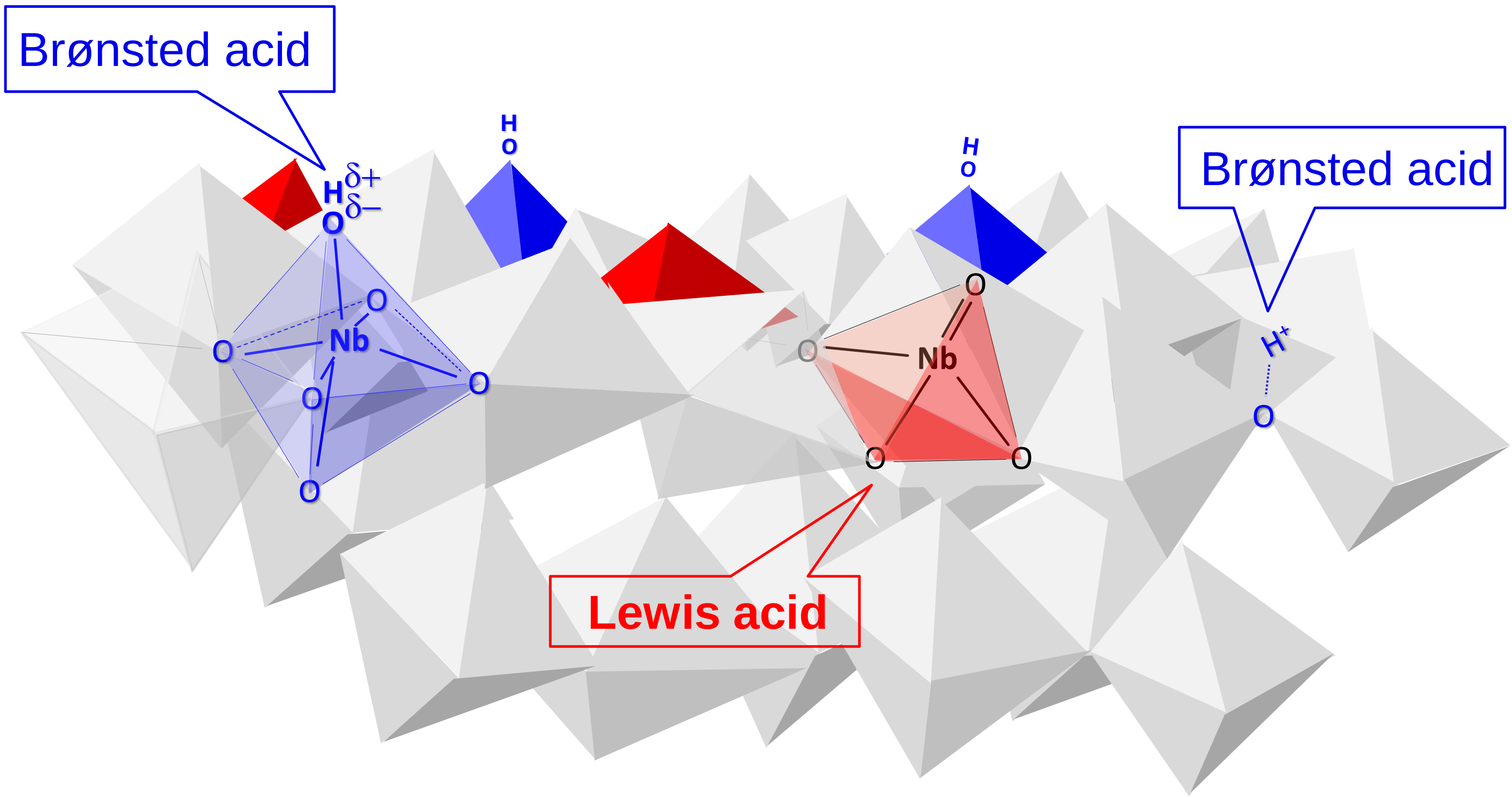
HMF

Furan dicarboxylic acid

What is "niobic acid ($Nb_2O_5{\cdot}nH_2O$)"

$Nb_2O_5{\cdot}nH_2O$

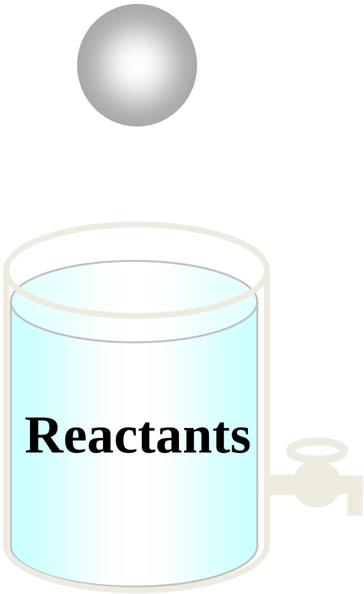
- was well-studied by Prof. Kozo Tanabe, a pioneer for "solid acid catalyst".
- is a strong Brønsted acid catalyst with its acidity comparable to an aqueous 70% H_2SO_4 solution（H_0=-5.6）.
- is one of isopoly acids ($H_8Nb_6O_{19}$) with Bronsted acidity and Lewis acidity.
- has water-tolerant Lewis acid sites available for sugar conversion.



Prof. Kozo Tanabe

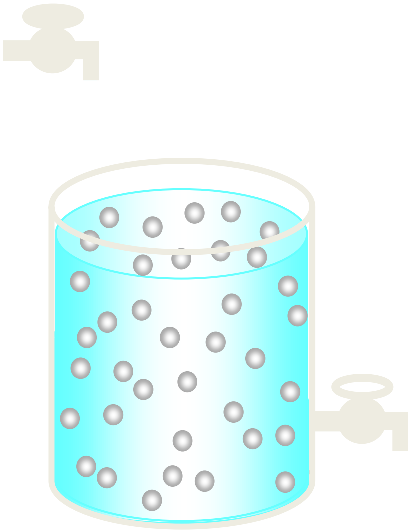
1. T. Iizuka, K. Ogasawara, K. Tanabe, *Bull. Chem. Soc. Jpn.*, **56**, 2927 (1983)
2. K. Tanabe, S. Okazaki, *Appl. Catal. A*, **133**, 191 (1995)

If we have solid “sulfuric acid” (Cheap, high acidity, and high stability)······



- Safety for handling

- Safety for handling
- Catalyst is easily separable from reaction mixture



- Safety for handling
- Catalyst is easily separable from reaction mixture
- Highly reusable

Neutralization is inevitable in H_2SO_4 process.

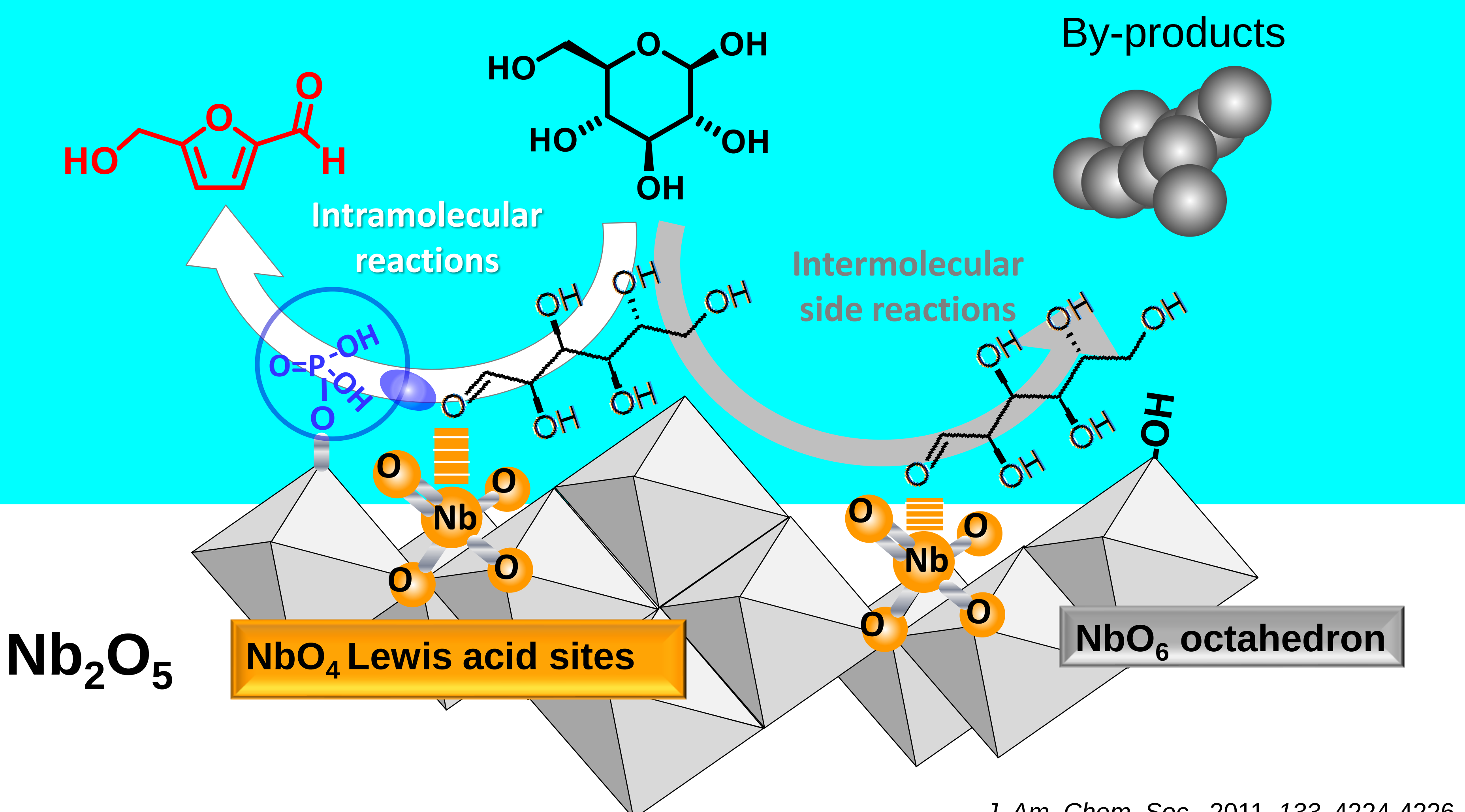
$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4\downarrow + CO_2\uparrow + 2H_2O$

→ 1 kg of H_2SO_4 produces 1.4 kg of Na_2SO_4 (acid waste).

HMF production with phosphate/$Nb_2O_5 \cdot nH_2O$

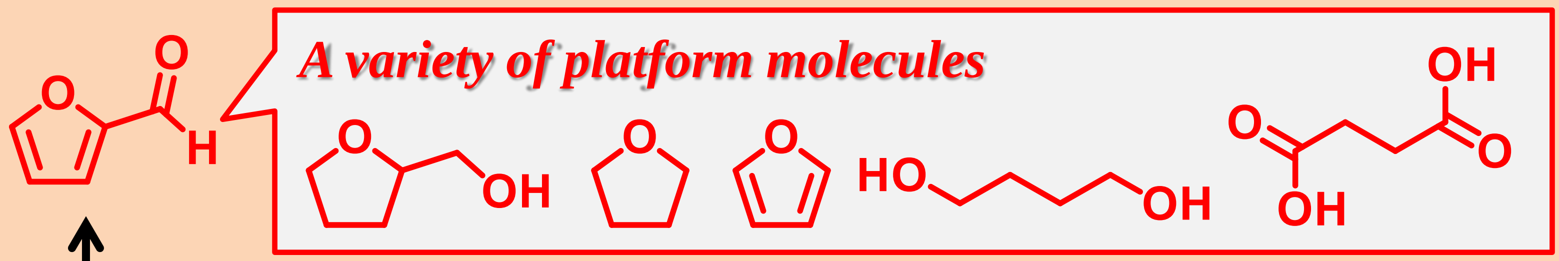
- High activity at mild reaction temperatures
  Nb_2O_5 >> HCl, H_2SO_4, zeolites, etc…

Water-THF



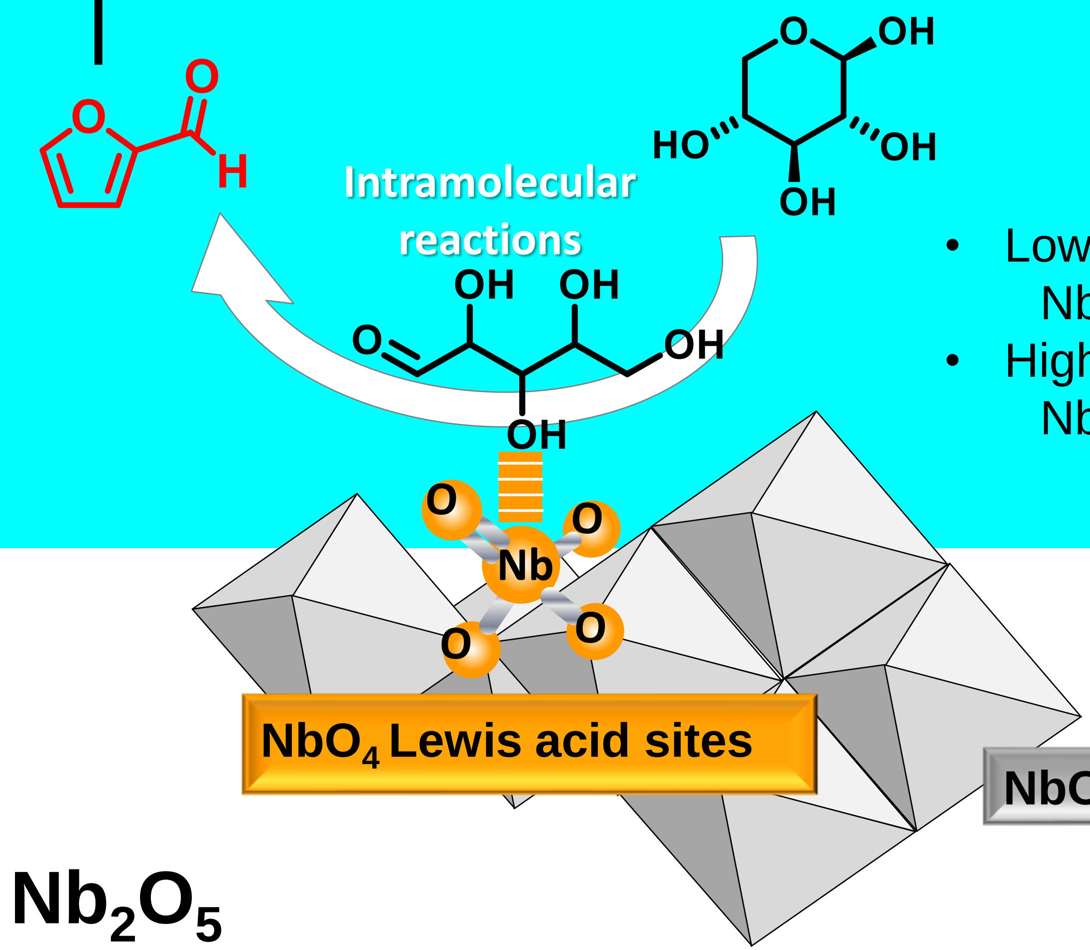
J. Am. Chem. Soc., 2011, *133*, 4224-4226.

Furfural production with bare $Nb_2O_5 \cdot nH_2O$



Toluene

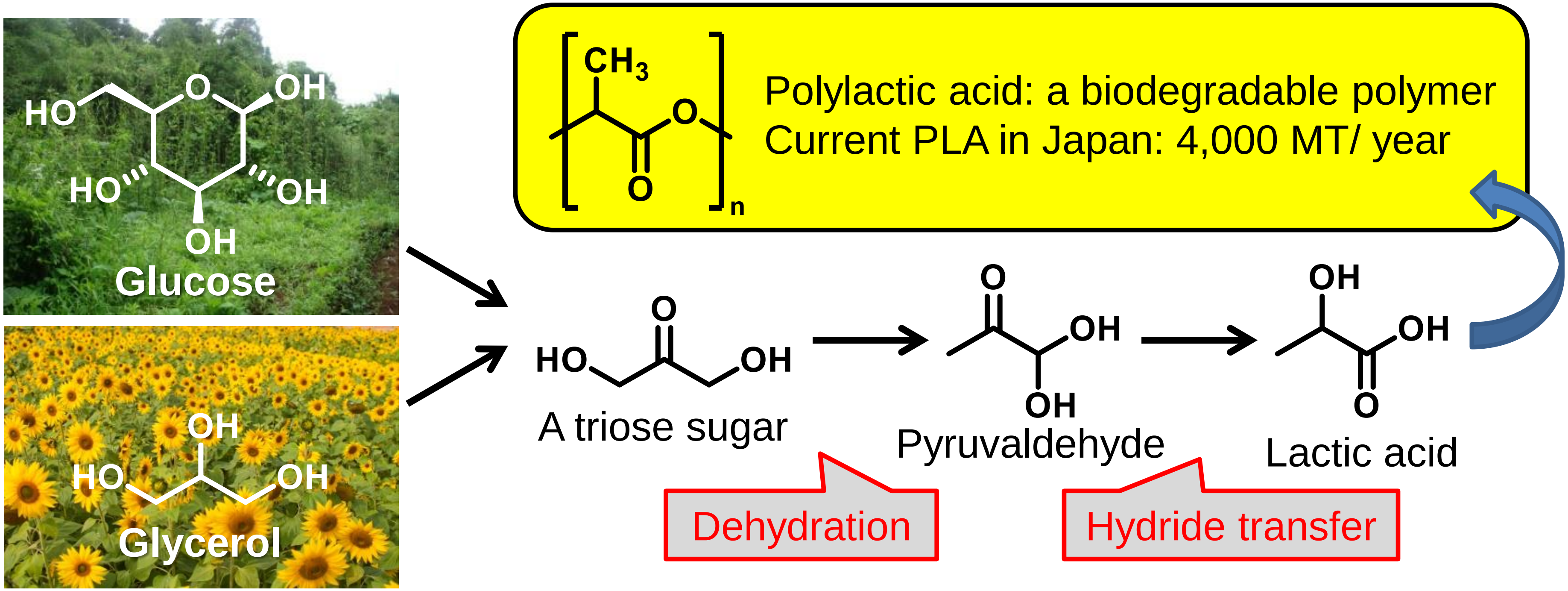
Water

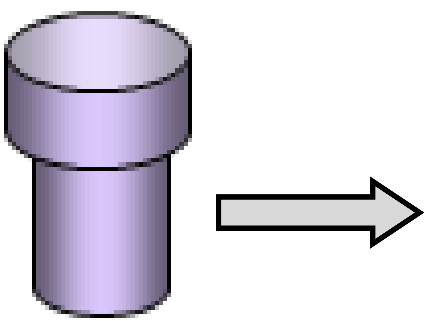


- Low activation energy (kJ mol^{-1})
  Nb_2O_5 (86), HCl (150), H_2SO_4 (161)
- High reaction rate (mmol g^{-1} h^{-1})
  Nb_2O_5 (2.1), HCl (0.6), H_2SO_4 (0.3)

ACS Catal., 2017, *7*, 2430-2436.

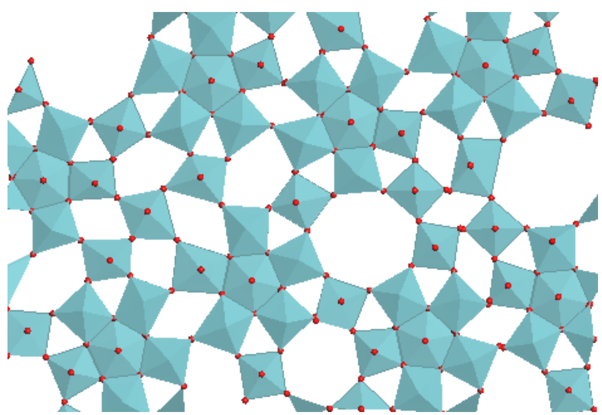
Lactic acid formation from a triose over deformed ortho-Nb_2O_5





Niobium oxalate (CBMM)

A deformed orthorhombic Nb_2O_5

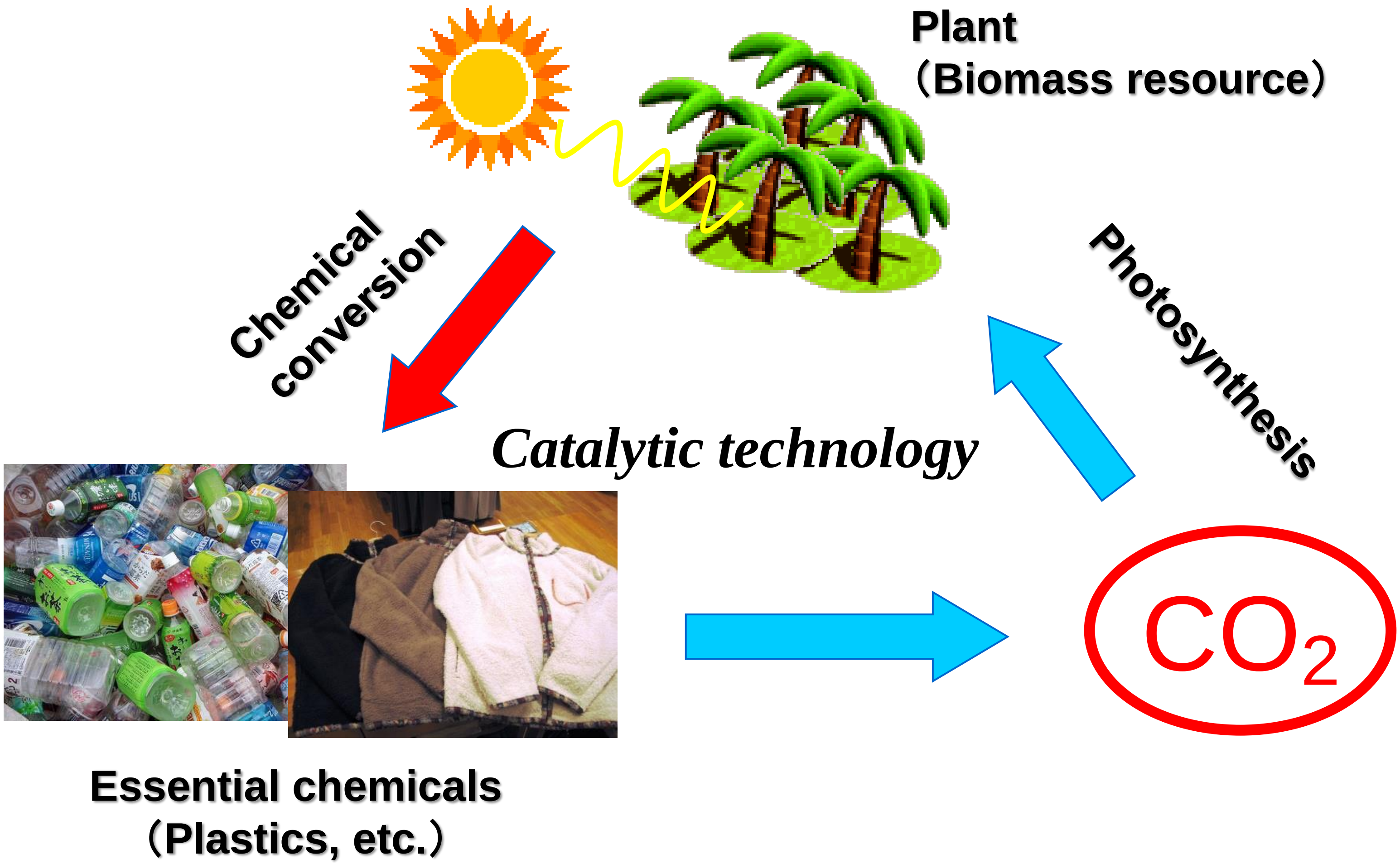


The pentagonal units are connected to each other by octahedral NbO_6 linkers, forming 7-membered ring micropores.

- Surface area
  Ortho-Nb_2O_5 ≈ $Nb_2O_5 \cdot nH_2O$
- Acid site
  Ortho-Nb_2O_5 >> $Nb_2O_5 \cdot nH_2O$

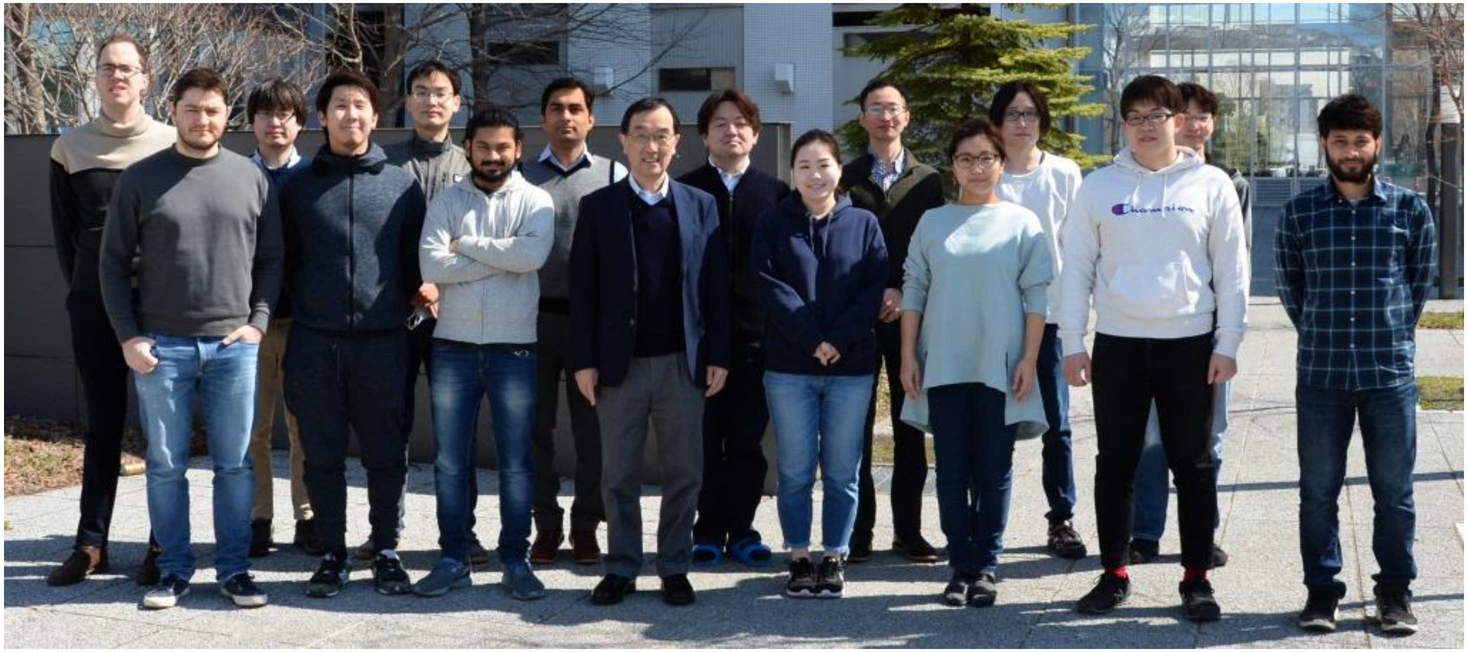
ACS Catal., **2018**, *8*, 283-290

Perspective: catalytic technology for sustainable society



- *Renewable carbon resources (non-edible biomass)*
- *Catalytic technology using heterogeneous catalysts for sustainable chemical production*
- *Continuous studies for unique catalysis of Niobium materials in biomass conversion*
- *Continuous friendship (Catalysis society of Japan and CBMM/Sojitz) for reference catalysts (Niobium oxide hydrate, Niobium oxide optical grade, Ammonium Niobium Oxalate)*

Acknowledgement:



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- Fostering Joint International Research (B)

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Network Joint Research Center for Materials and Devices