

Mathematical Modelling of the Aqueous Phase Reforming of Sorbitol

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29th October 2014

OUTLINE

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Introduction

Hydrogen energy is one of the most promising options both for energy source and non-petroleum derived chemicals.

Aqueous Phase Reforming (APR) is an alternative option for energy savings as it is operated at significantly lower temperature (100 - 150°C).

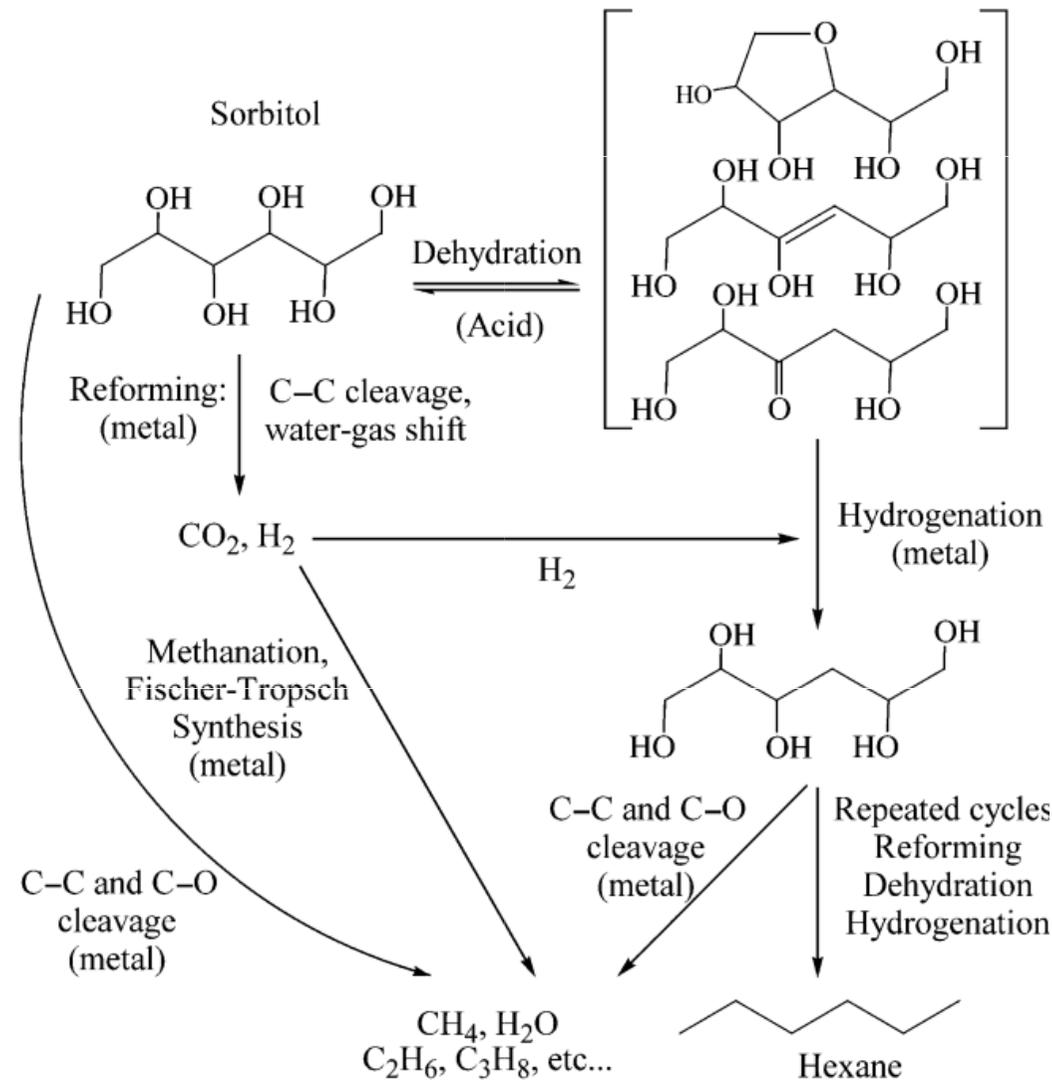
APR produces less tars and chars. The process encompasses steam reforming and water gas shift (WGS) reactions.

Sorbitol is used as a starting material model for APR of biomass oxygenates. Sorbitol is generated from the reduction of glucose. It is used in medical, healthcare, cosmetics and food. It has the same number of C-C and C-O bonds.

Mono and bimetallic catalysts based on Ni and Pd supported on Al₂O₃, ZrO₂ and CeO₂ were used.

The lack of established rate constants for 260+ reactions, the combination of gas-phase and liquid-phase and the non-linearity of kinetic process due to surface adsorption, set huge barriers to achieving a well-established kinetic model.

Sorbitol aqueous phase reforming [Cortright et al. 2002, Huber et al. 2010, Chheda et al. 2007]



Objectives

Study the kinetics of APR sorbitol into gaseous products over temperatures between 100°C and 150°C, $C_6H_{14}O_6(l) + 6H_2O(l) \longrightarrow 6CO_2(g) + 13H_2(g)$

Ni and Ni-Pd catalysts supported on γ -Al₂O₃, ZrO₂ and CeO₂

A reduced kinetic model, which counts for all the gaseous compounds but a limited number of the liquid compounds which can be experimentally accessible.

The model relies on a lumping approach of the liquid-phase intermediates into a single and artificial intermediate which can represent any intermediate in the liquid phase.

Model results and experimental measurements will be compared along with the identification of the relevant reactions in the overall kinetics of the APR of sorbitol.

Experimental

Catalyst Preparation

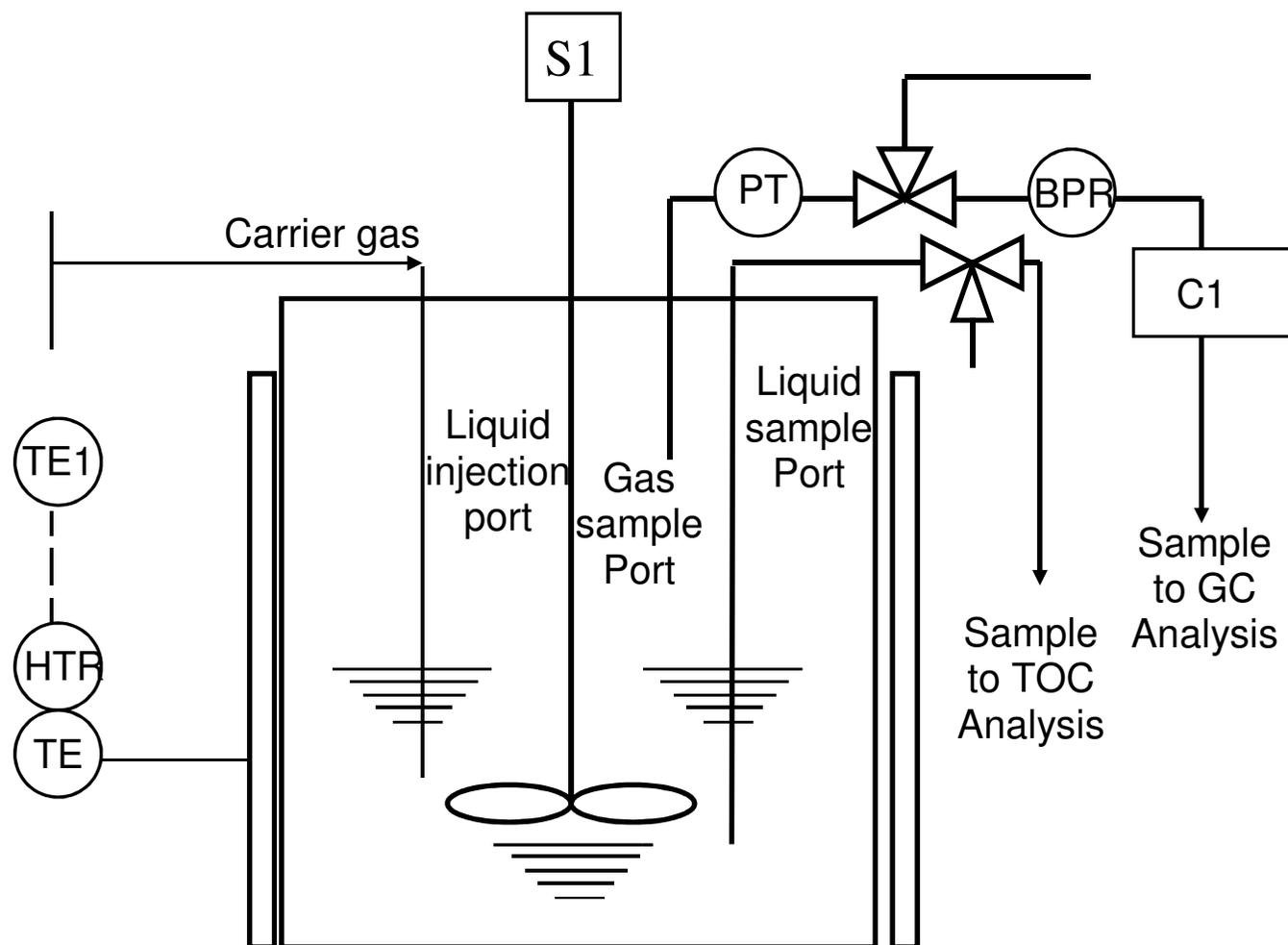
The catalysts were prepared by wet impregnation.

The supports used were γ -phase aluminum oxide 206 (Alfa Aesar, 20 nm APS powder), cerium (IV) oxide (Alfa Aesar, 15-30 nm APS powder) and 207 zirconium (IV) oxide (Alfa Aesar, 30-50 nm APS powder) while the precursor solutions were 208 nickel (II) nitrate hexahydrate (Aldrich) and palladium (II) chloride (Aldrich).

Catalyst Characterization

- Temperature-programmed reduction (TPR): to inspect catalyst reducibility, check free and fixed nickel, hydrogen uptake + temperature.
- CO Chemisorption: identify active metal sites, catalyst CO uptake, dispersion and particle size
- Temperature-programmed desorption and Oxidation (TPD and TPO): adsorption/desorption isotherms, identify carbon deposits (CO, CO₂) and H₂. To identify dehydrogenation, WGS, hydrogenation etc.
- Scanning and Transmission electron microscopies (SEM and TEM): to identify crystal shapes and clusters for monometallic and bimetallic, fresh and spent catalysts.

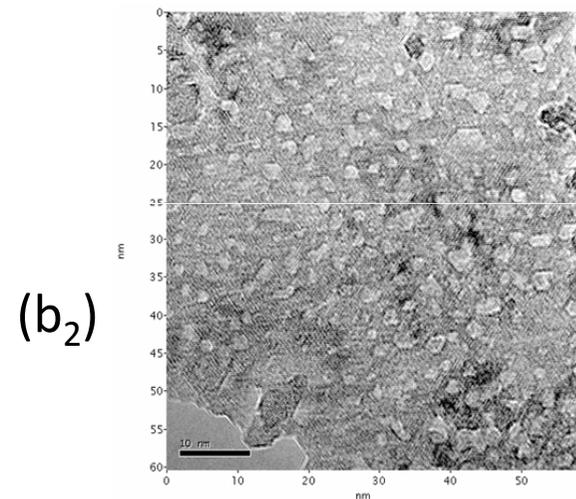
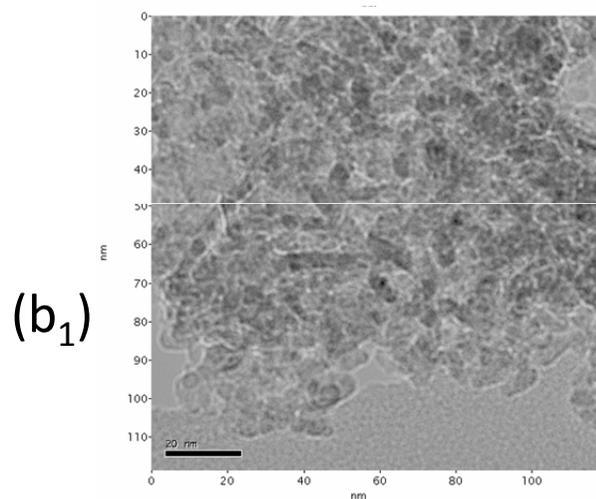
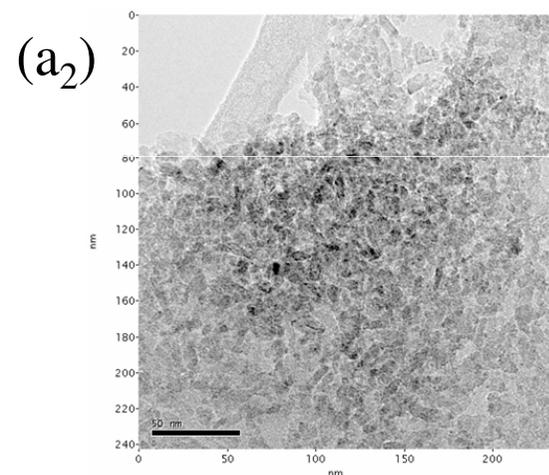
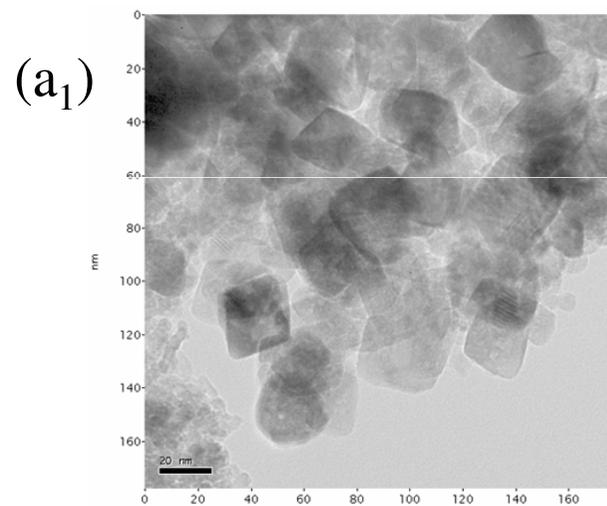
Apparatus:



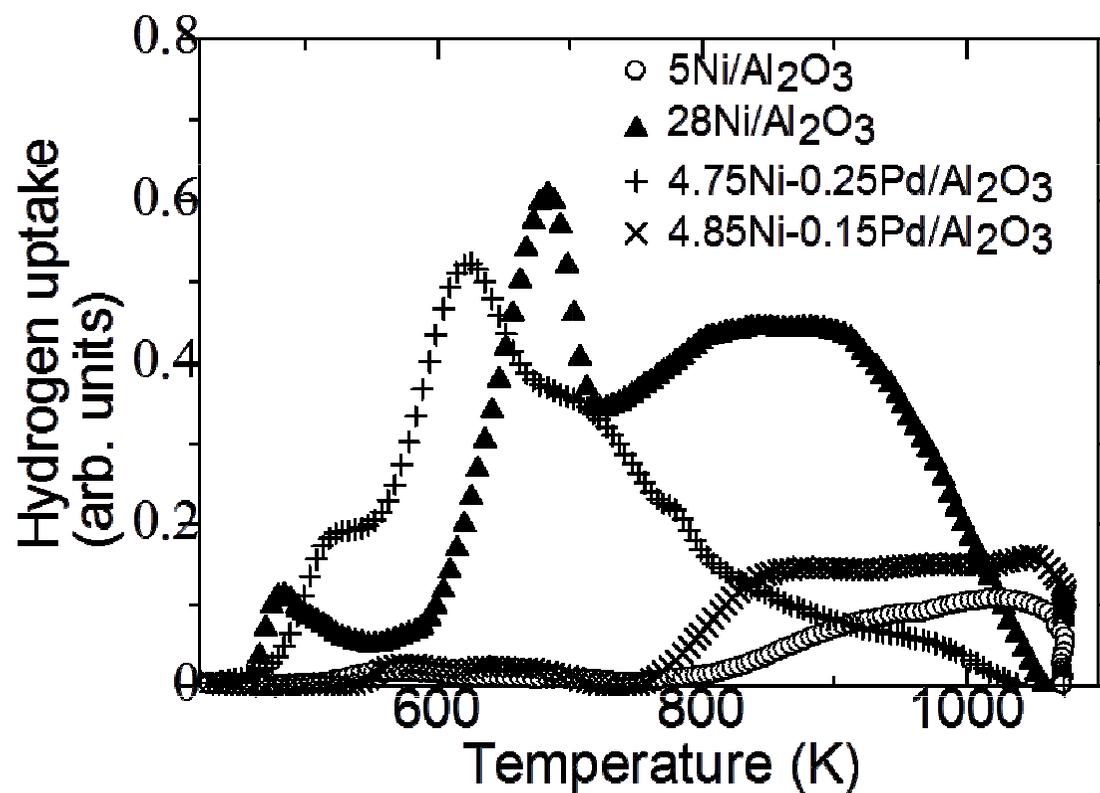
Experimental set up

HTR = Heating Jacket, TE= Thermocouple for the heating jacket, PT: Pressure transducer, TE1= Thermocouple temperature inside the reactor
 S1= Stirrer, C1: Cylinder filled with silica gel, BRP: Back-pressure regulator

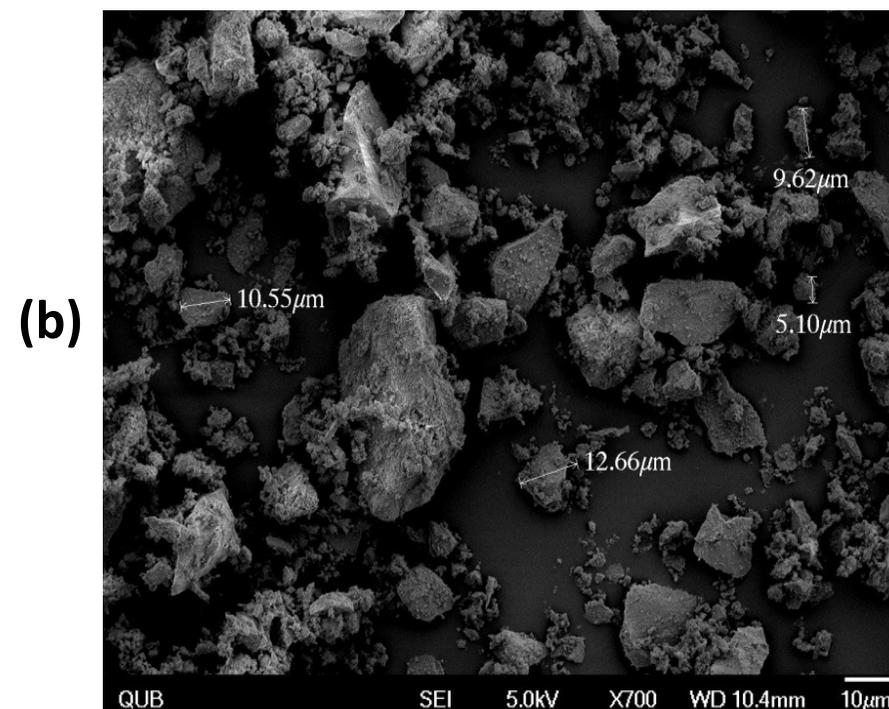
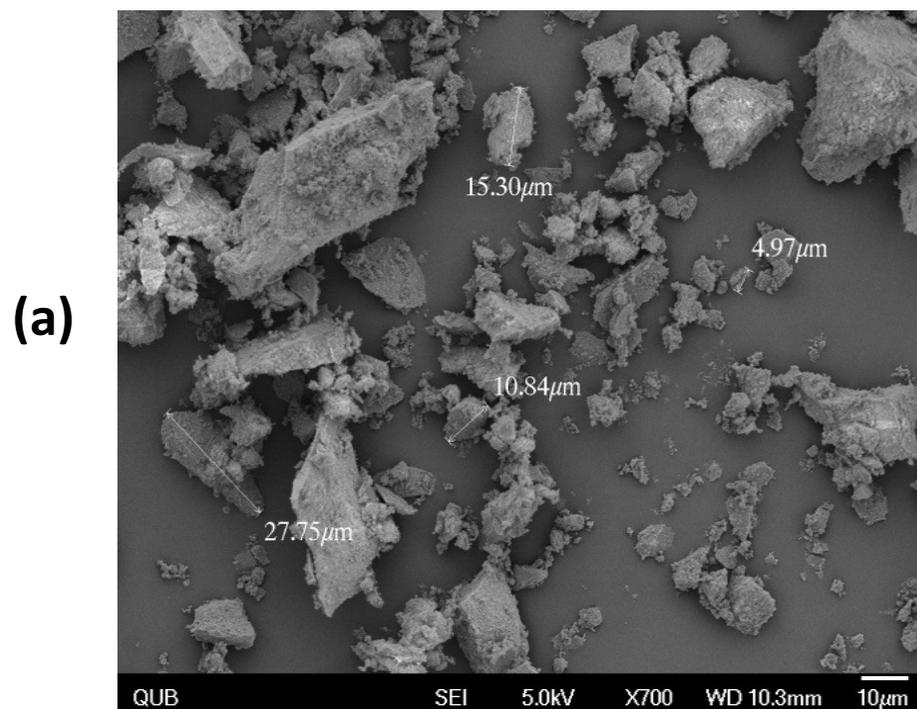
Results and Discussion



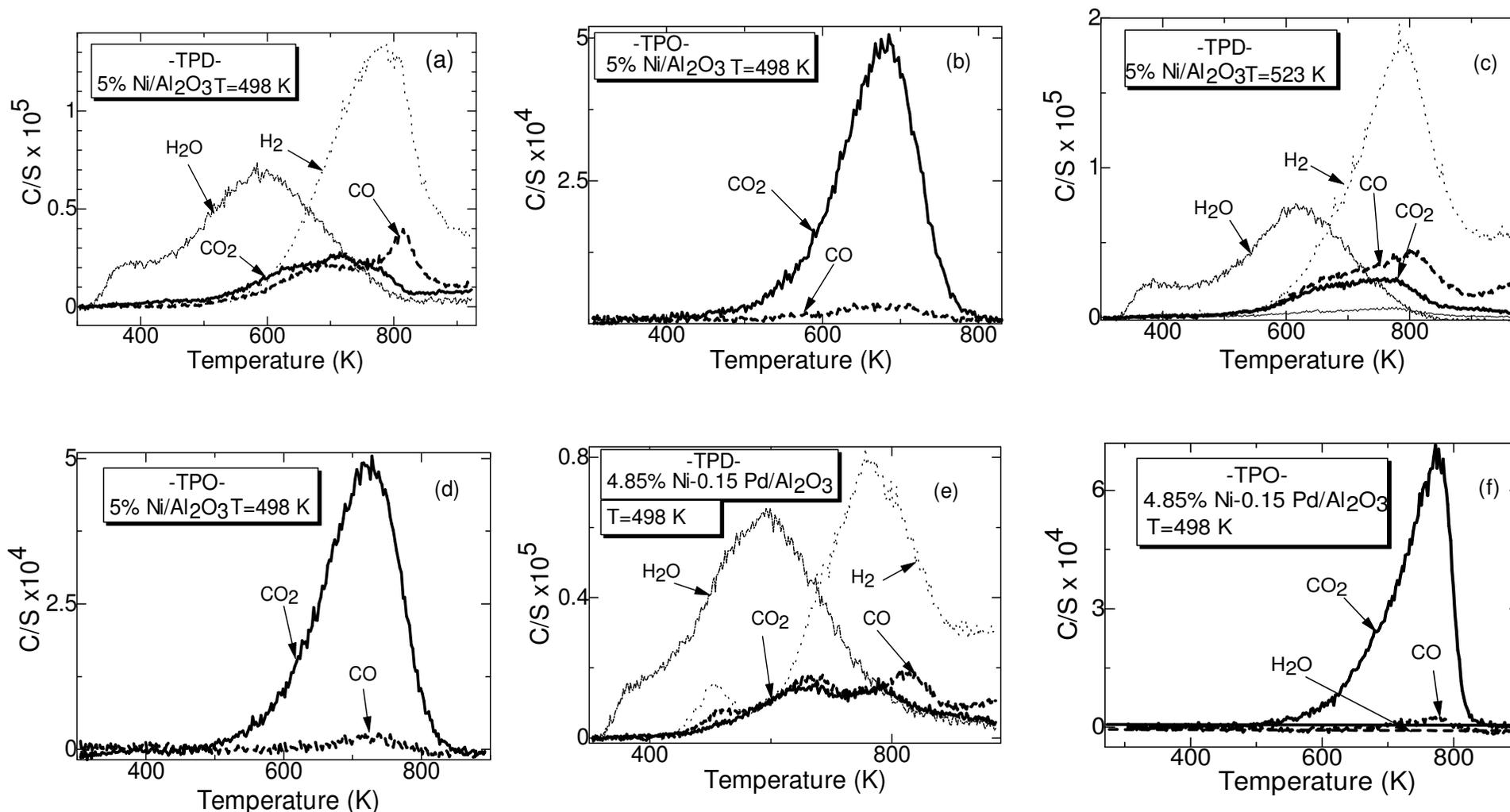
TEM images of fresh (a₁) and spent (a₂) monometallic catalyst 28%Ni/Al₂O₃ catalyst and fresh (b₁) and spent (b₂) bimetallic catalyst 4.75%Ni-0.25%Pd/Al₂O₃ catalyst



TPR profiles of mono and bimetallic catalysts supported on γ - Al_2O_3



**SEM images of fresh (a) 28%Ni/Al₂O₃ catalyst and (b) 4.75%Ni-0.25%Pd/Al₂O₃ catalyst.
No internal mass transfer resistance**



TPD profiles of spent mono- and bimetallic catalysts (a) TPD of 5%Ni/Al₂O₃ at 498 K, (b) TPO 5%Ni/Al₂O₃ at 498 K, (c) TPD 5%Ni/Al₂O₃ at 523 K (d) TPO 5%Ni/Al₂O₃ at 523 K, (e) TPD of 4.85%Ni-0.15%Pd/Al₂O₃ at 498 K, (f) TPO 4.85%Ni-0.15%Pd/Al₂O₃ at 498 K

Mathematical Modeling:

The aim of this kinetic modeling is to identify the reaction pathways leading to the formation of the gaseous products and to quantify rates of formation for different activities of monometallic and bimetallic catalysts and temperature from 473 to 523 K.

The catalytic tests and TPD-TPO analysis focused exclusively on experimental validation of the mechanism involved in the APR of sorbitol. The contribution of side reactions such as CO₂ hydrogenation (equation 3) and hydrodeoxygenation (equation 4), dehydrogenation (equation 5), decarbonylation (equation 6) and hydrodeoxygenation-decarbonylation by CH₄ release (equation 7) on the overall APR of sorbitol were not precisely quantified.

The APR of sorbitol follows two paths (3-5) and (6-9)

- *Generation of intermediate*



- *Reforming and WGS by cleavage of C-C and C-H bonds*



- *CO₂ methanation and Fisher-Tropsch reactions*



- *Oxygenated intermediates by hydrodeoxygenation (dehydration and hydrogenation)*



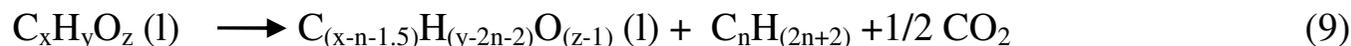
- *Oxygenated intermediates by dehydrogenation*



- *Oxygenated intermediates by decarbonylation and WGS*



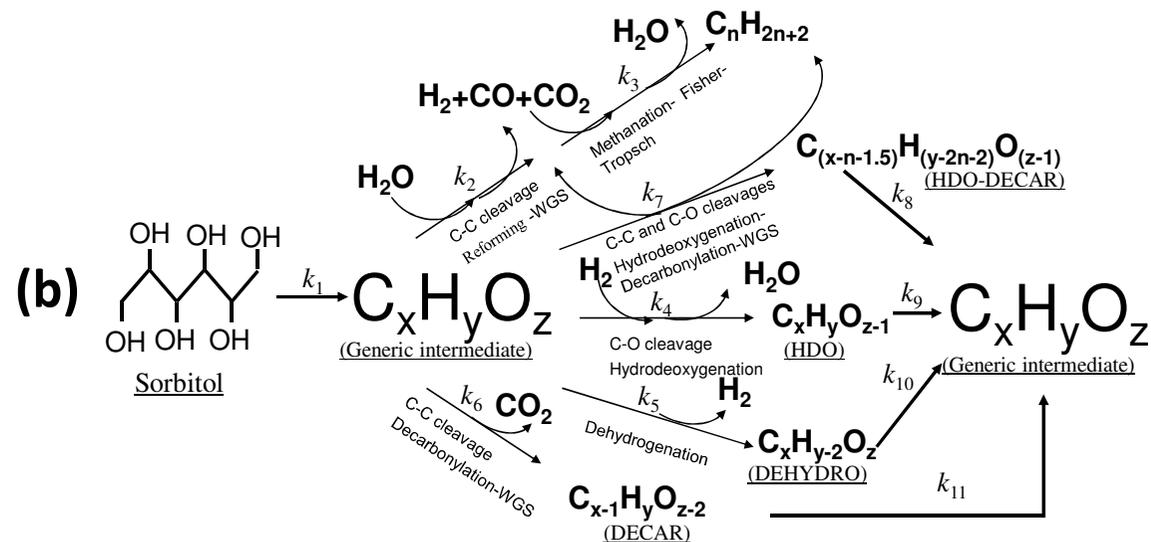
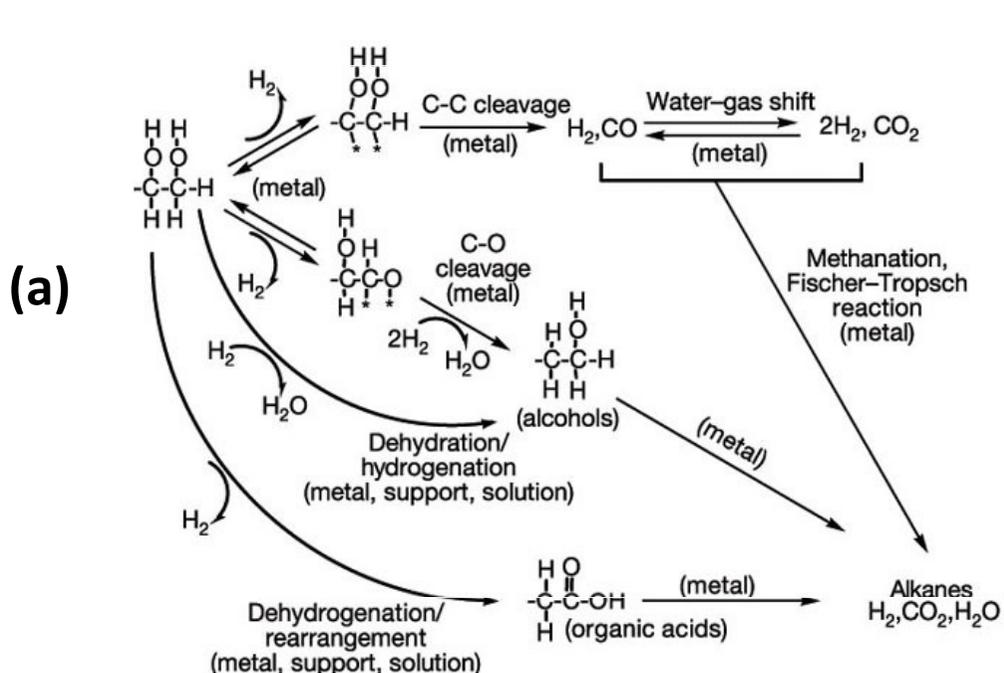
- *Alkanes by hydrodeoxygenation-decarbonylation*



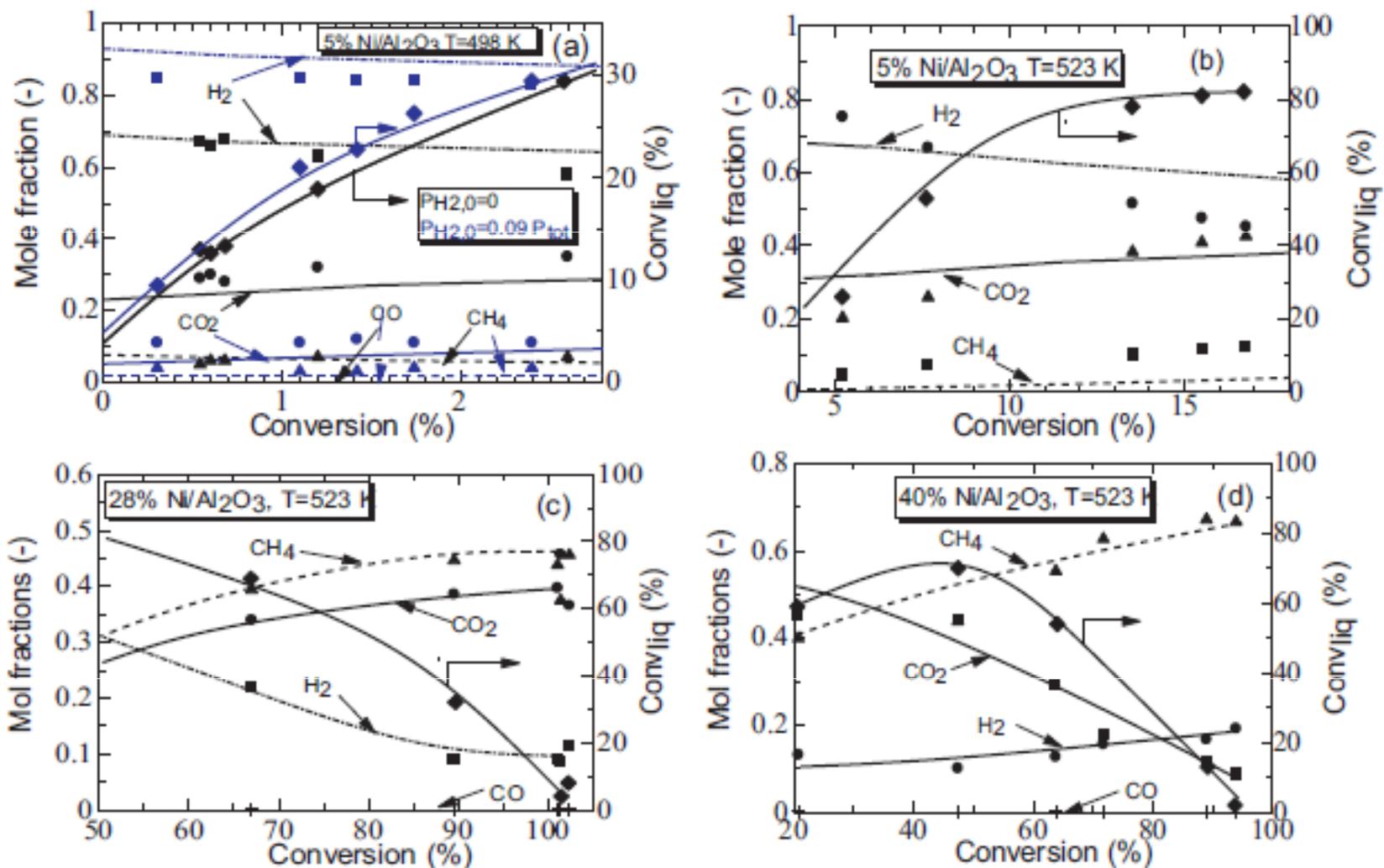
Kinetic Modeling Assumptions:

- Rate equation for each reaction was assumed to be first order in coverage of each species in the reaction.
- Reforming, hydrodeoxygenation, dehydration, decarbonylation and hydrodeoxygenation-decarbonylation towards alkanes were assumed to take place on the surface of the catalyst by a series of irreversible steps since the equilibrium constants for these steps were rather large in view of the very favorable thermodynamics.
- The validity of the model was tested by fitting and tuning the proposed rate equations to the experimental data. We assume that the most abundant surface species are $C_6H_{14}O_6$, H_2 , H_2O , CO_2 and CH_4 , and therefore, alkanes in equation 7 will be represented by CH_4 .
- No mass transfer limitations, isomerization, thermal degradation or condensations were considered in the modeling scheme

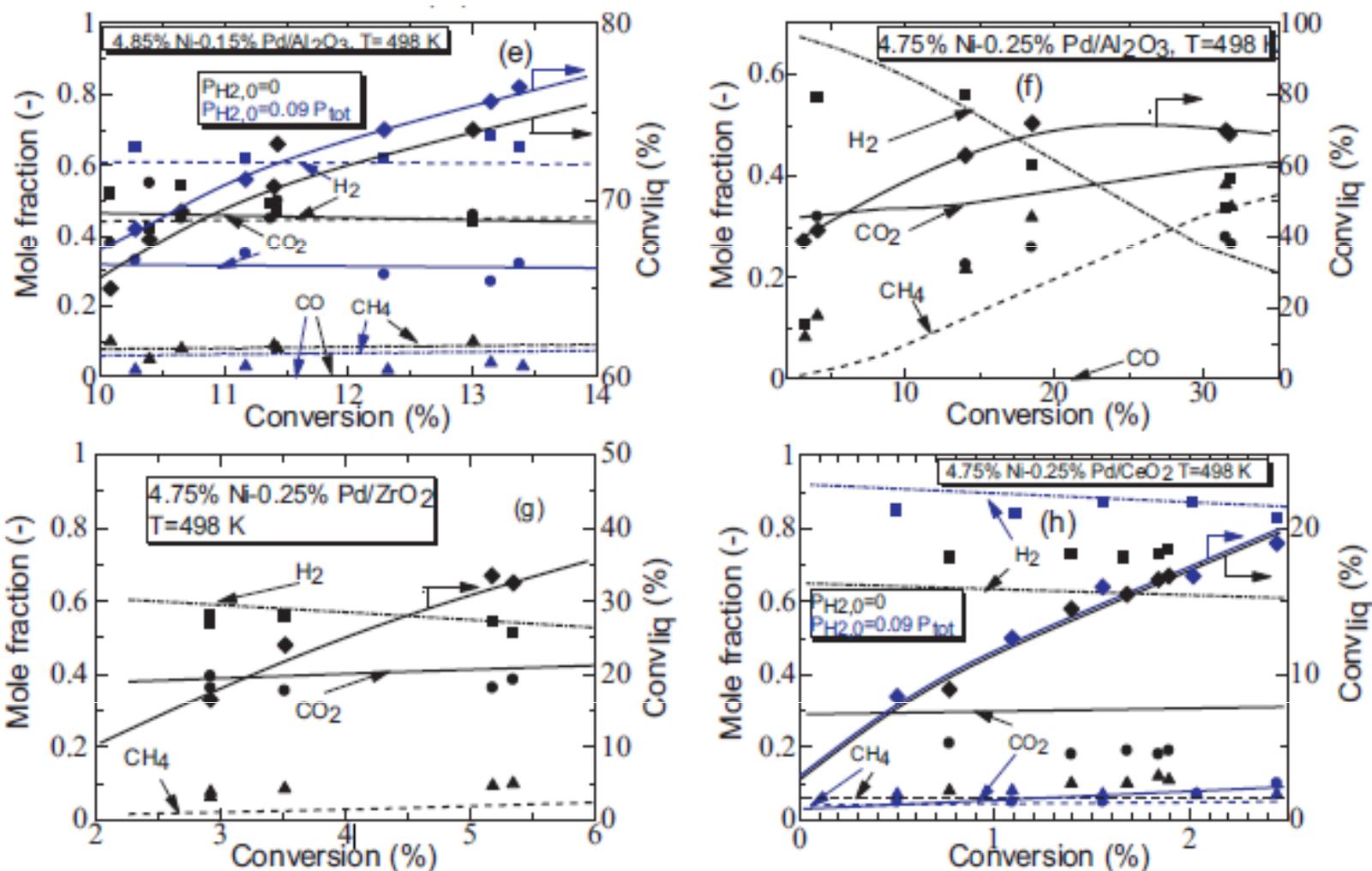
Mechanisms:



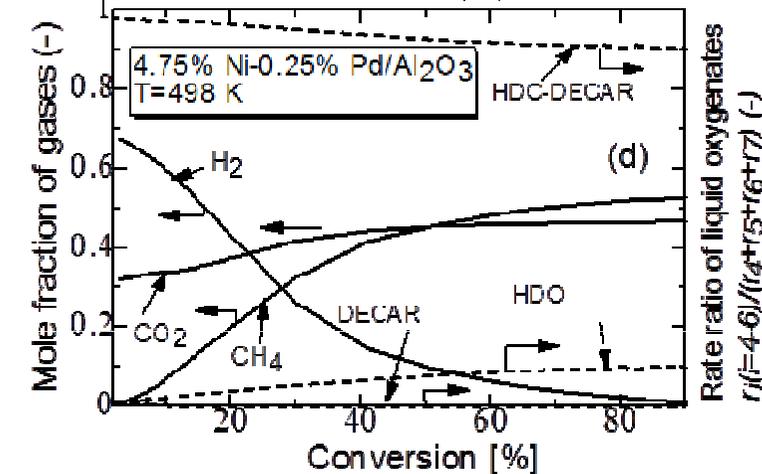
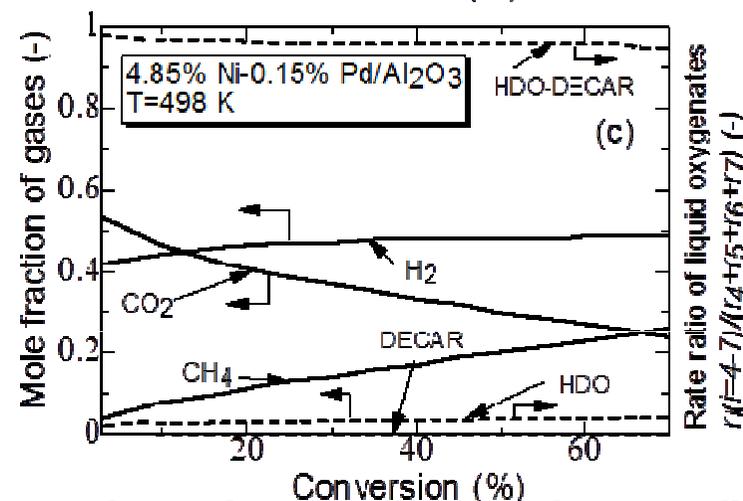
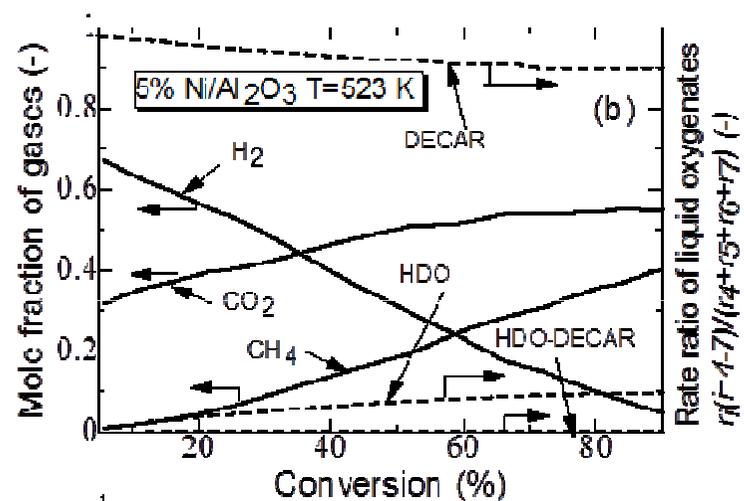
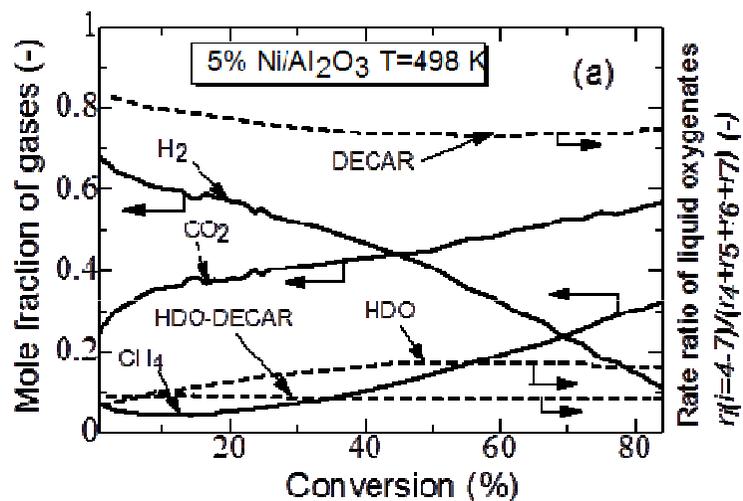
Path lumping for sorbitol aqueous phase reforming over solid catalysts
 (a) Detailed model ¹, ¹⁰ and ⁸; (b) Path lumping model



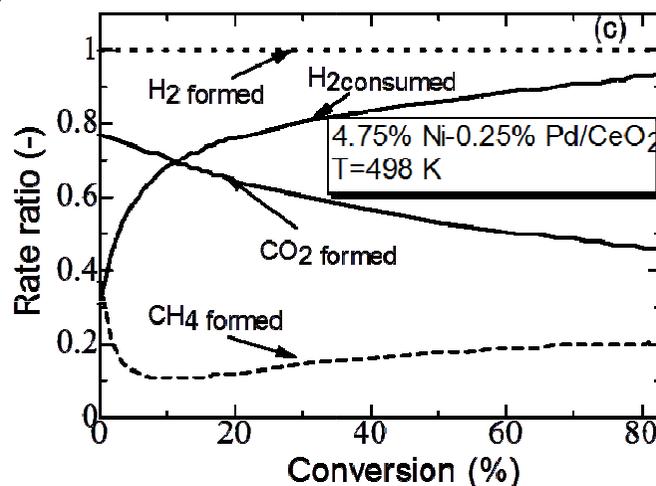
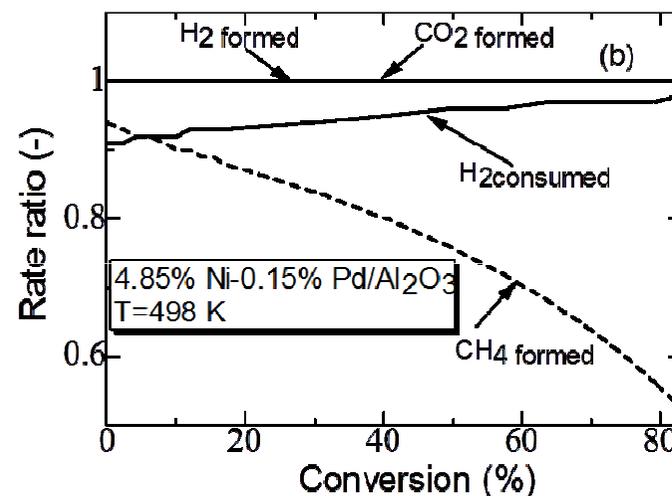
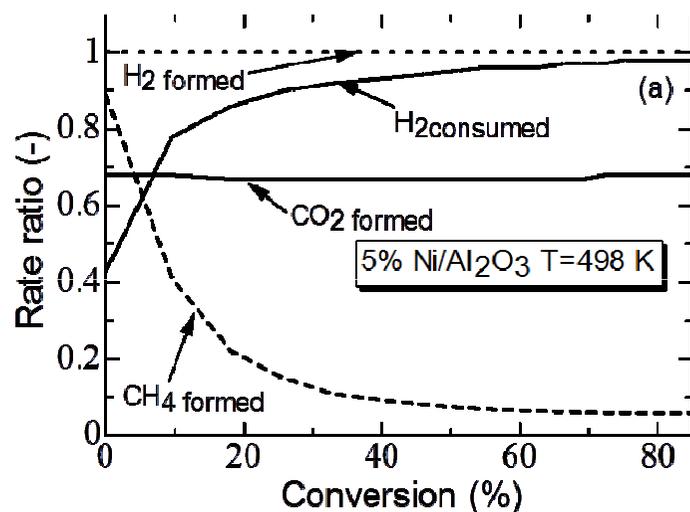
Product mole fraction profiles versus conversion, (a) 5%Ni/Al₂O₃ at 498 K, (b) 5%Ni/Al₂O₃ at 523K, (c) 28% Ni/Al₂O₃ at 523 K, (d) 40%Ni/Al₂O₃ at 523K, • CO₂, ▲ CH₄, ■ H₂, + CO, ◆ Conversion to products



Product mole fraction profiles versus conversion, (e) 4.85%Ni-0.15%Pd/Al₂O₃ at 498 K, (f) 4.75%Ni-0.25%Pd/Al₂O₃ at 498 K, (g) 4.75%Ni-0.25%Pd/ZrO₂ at 498 K, and (h) 4.75%Ni-0.25%Pd/CeO₂ at 498K, ● CO₂, ▲ CH₄, ■ H₂, + CO, ◆ Conversion to products



Prediction of product mole fraction profiles in the gaseous phase and rate ratios of liquid oxygenates versus conversion, (a) 5%Ni/Al₂O₃ at 498 K, (b) 5%Ni/Al₂O₃ at 523K, (c) 4.85%Ni-0.15%Pd/Al₂O₃ at 498 K, (d) 4.75%Ni-0.25%Pd/Al₂O₃ at 498 K



Model predictions of rate ratios profiles of H₂ formed ($r_2/(r_2+r_5+r_6)$), CO₂ formed ($r_2/(r_2+r_6+r_7)$), CH₄ formed ($r_3/(r_3+r_7)$) and H₂ consumed ($r_3/(r_3+r_4)$) versus conversion, (a) 5%Ni/Al₂O₃ at 498 K, (b) 4.85%Ni-0.15%Pd/Al₂O₃ at 498 K, and (c) 4.75%Ni-0.25%Pd/CeO₂ at 498K

Conclusions

This work presents the first quantitative kinetics model for the catalytic APR of biomass-derived oxygenates such as sorbitol. The variety of liquid and gaseous products and their potential use as blending fuels and fuel additives directed the quantitative kinetic model to be investigated over a lumping scheme rather than focusing on each component separately.

The model describes the complex path of APR of sorbitol by a generic intermediate that forms the gaseous products via two routes. The first leads to gaseous phase products over reforming, WGS reactions and CO or CO₂ methanation and the second leads to liquid and gaseous phase products over hydro-deoxygenation (dehydration and hydrogenation), decarbonylation, dehydrogenation and hydrodeoxygenation - decarbonylation towards alkane reactions.

The kinetic model was tested at temperatures ranging from 473 K to 523 K, initial concentrations of sorbitol in water of 5% and 10% and using monometallic Ni and bimetallic Ni-Pd catalysts supported on γ -Al₂O₃, ZrO₂ and CeO₂.

The Model results are in agreement with experimental data.

Thank You

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