HCHAIB
Hydrogenation of Carboxylic Acids Issued from Biomass (CP2D 2009)

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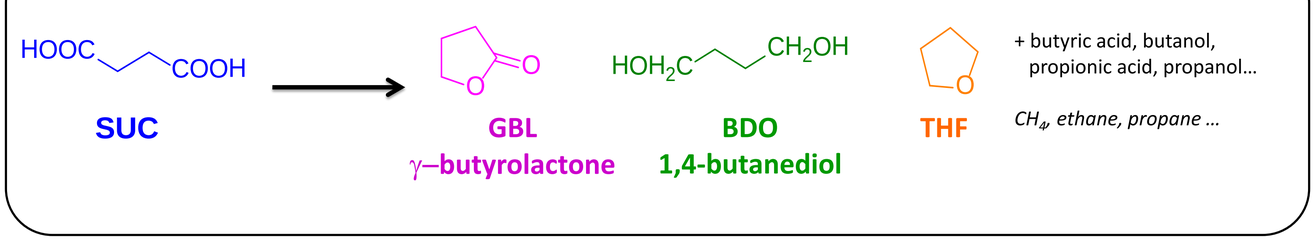
OBJECTIVES:

- Evaluation of bimetallic catalysts **xwt%Re-2wt%Pd/TiO_2** in the aqueous phase catalytic hydrogenation of SUC
- Influence of preparation mode on activity of catalysts and selectivity to BDO



PREPARATION OF CATALYSTS

Monometallic catalyst 2wt%Pd/TiO_2

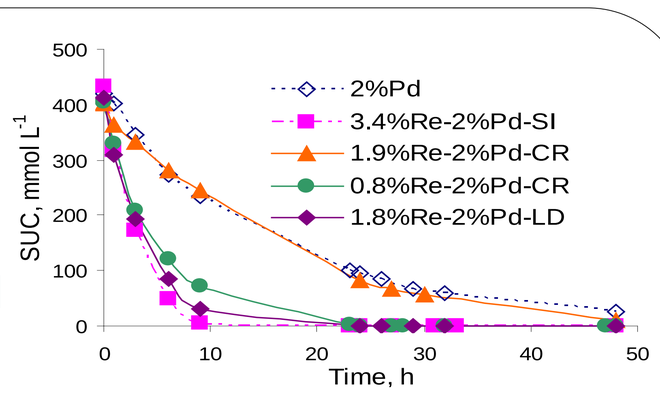
Support TiO_2 DT51 (S_{BET}=90 m²/g)

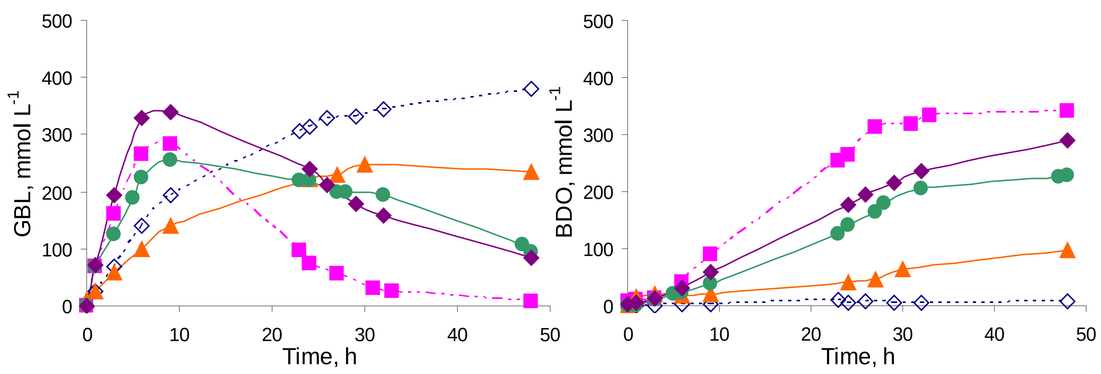
Deposition-precipitation using K_2PdCl_4 and KOH
Reduction by H_2 at 300°C-3h

Bimetallic catalyst xwt%Re-2wt%Pd/TiO_2
Aqueous solution NH_4ReO_4
using the monometallic catalyst

Successive impregnation (SI)	Catalytic reduction (CR)	*In-situ* treatment (liquid phase deposition)
• Impregnation • Evaporation and drying • Activation by H_2 at 450°C-3h **3.4%Re-Pd-*SI***	• Surface redox reaction: nH_{ads}-(Pd_s) + Re^{7+} -> Re^{7-n}-(Pd_s) + (7-n)H^+ • Activation by H_2 at 450°C-3h **0.8 or 1.9 %Re-Pd-*CR***	• In the reactor, addition of precursor salt of Re. • Activation by H_2 at 150 bar, 160°C, 1h. **1.8%Re-Pd-*LD***

SUCCINIC ACID HYDROGENATION





CR method (~1%Re) < LD (~2%Re) < SI (~4%Re)

CHARACTERIZATIONS

Dispersion

Cyclohexane dehydrogenation (CD)
= Structure insensitive (Re inactive)

Metal	H/Pd (%)	CD activity 270°C ($mol.h^{-1}.g^{-1}_{Pd}$)
2%Pd	27	2.9
0.8%Re-2%Pd-*CR*	10	2.2
1.9%Re-2%Pd-*CR*	8	2.0
3.4%Re-2%Pd-*SI*	21	2.4

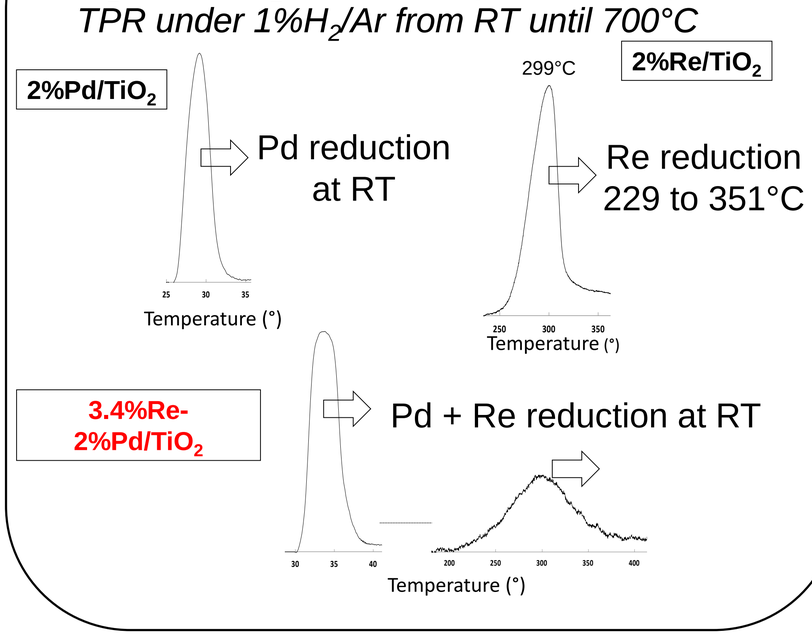
Addition of Re

↘ Pd accessibility
↘ Pd dehydrogenating activity

Re deposition onto Pd particles

TPR

O_2 300°C, N_2 at room temperature (RT), TPR under 1%H_2/Ar from RT until 700°C



XPS

2.6%ReO_4NH_4-Pd-*SI* → (Re^{7+})
2.6%Re-Pd-*SI* → (Re^{4+} + Re^{6+} + Re^{7+})
2.6%Re-Pd-*CR* → (Re^{4+} + Re^{6+} + Re^{7+})

In-situ reduction in XPS cell at 450°C under H_2 during 3h

30% Re^0 + 70%Re^{3+}

✓ Re is readily oxidized in air.
✓ After reduction *ex-situ*,
Re exists in different oxidation states.
✓ After reduction *in-situ* (H_2 at 450°C-3h),
only ~30% is reduced up to Re°, the rest is Re^{3+}

CONCLUSIONS

To obtain an optimum selectivity to BDO:
the ***SI*** method required a high amount of Re (3-4wt.%),
the ***CR*** and ***LD*** methods required lower loadings (0.6-0.9wt.% and 2wt.%, respectively).

Best selectivity to BDO = 90%

at total conversion

in the presence of 3.4%Re-2%Pd/TiO_2-*SI*

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