

Design Ni-based catalysts for value-added upgrading of a biomass-derivative

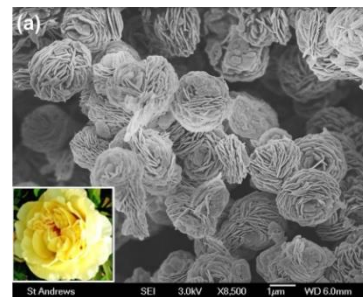


Zheng JIANG
z.jiang@soton.ac.uk

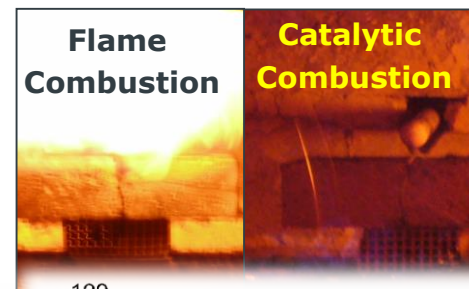
Energy Technology Group
Faculty of Engineering and the Environment

Research Projects

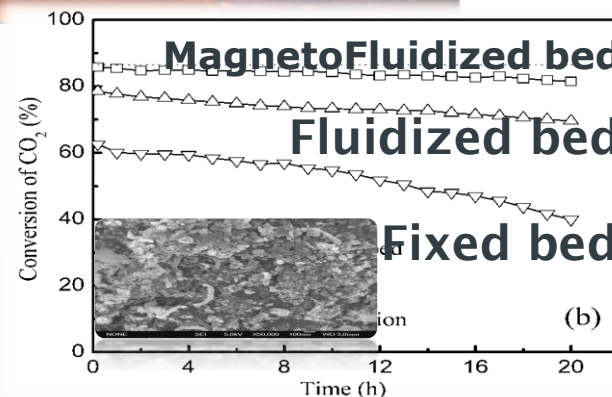
1. Semiconductor catalysts for Solar Energy Conversion



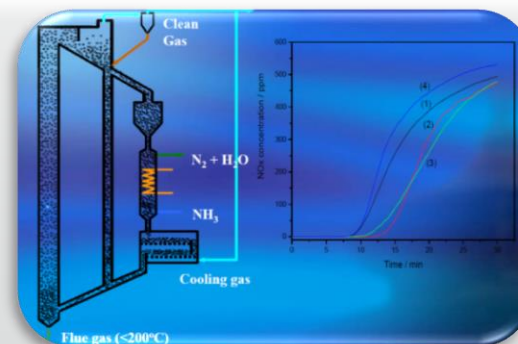
2. Clean Fossil Fuel 2.1 Efficiency



2.2 CO_2 Utilization via Biogas Upgrading via **PI**



3. **Hydrogenation** & Bio-oil Upgrading



Materials & Process

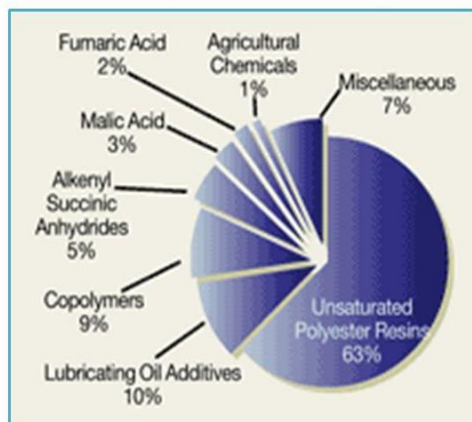
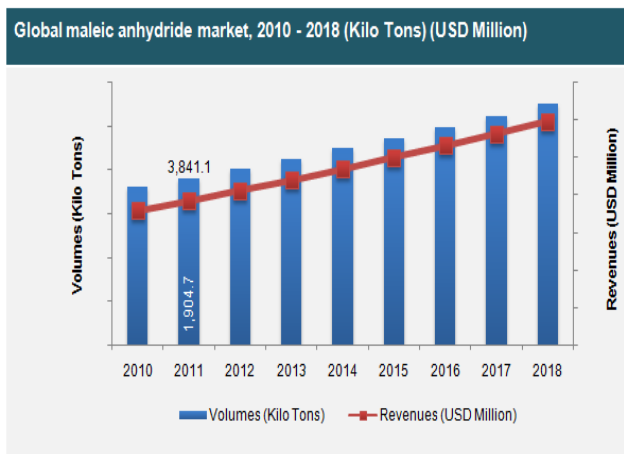
Environment

- 1. Background of MAH & Catalyst systems –Economy & Catalyst aspects**
- 2. Application of active Support**
- 3. Optimising Ni loading**
- 4. Tuning Ni electronic configuration**
- 5. Conclusion**

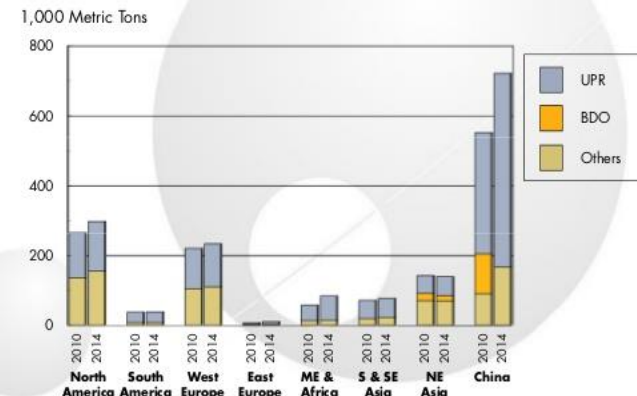
1. Background

- The market volumes of MA
- The sources of MA
- The catalysts for MAH
- **Chemical Process Engineering: gas- or liquid- phase?**
- Environmental impact

Economic driver for MAH



APIC 2015 WORLD PURE MALEIC ANHYDRIDE APPLICATION BY REGION 2010 & 2014



Global Price



<https://www.icis.com/Articles/2003/10/10/525310/chemical-profile-maleic-anhydride>

APIC 2015 CHINA MALEIC ANHYDRIDE SUPPLY & DEMAND



APIC 2015 WEST EUROPE MALEIC ANHYDRIDE SUPPLY & DEMAND



MA sources

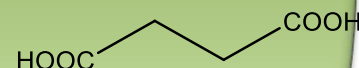
Coal

Oil

Biomass

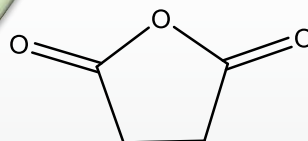
fermen
tation

dehydration



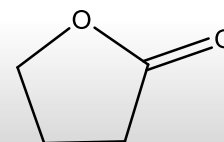
H₂

Catalyst



H₂/-H₂O

Catalyst



Can we use
sustainable H₂?

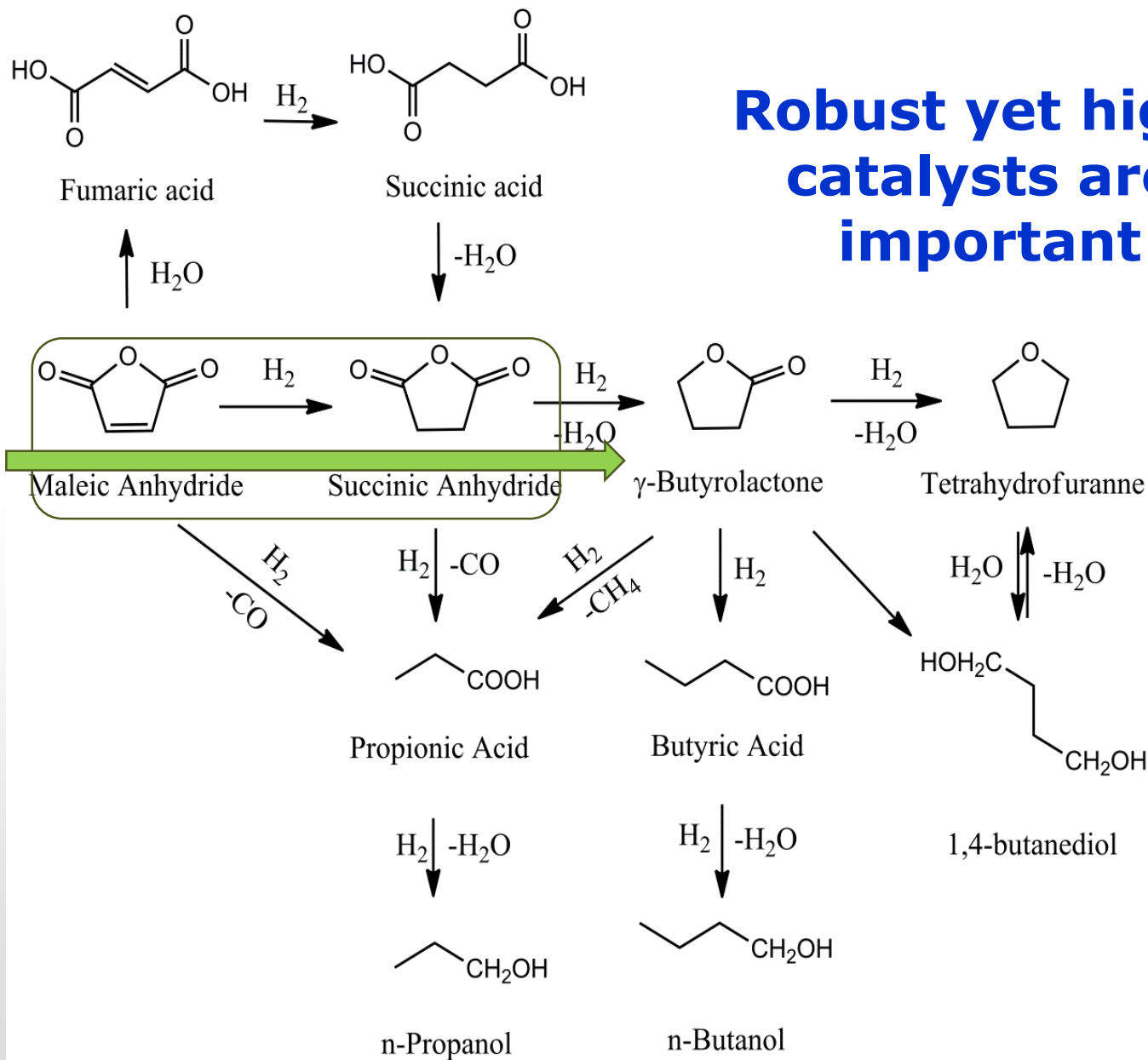
**Excessive
production**

**Sustainable
Process**

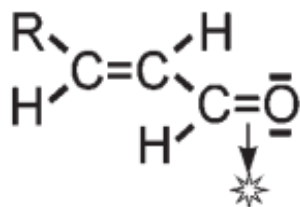
**High Value
Products**

Complexity of MAH: Selectivity

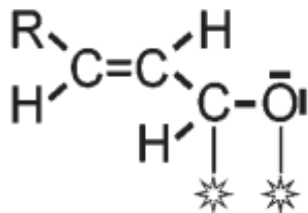
Robust yet highly selective catalysts are extremely important & desired



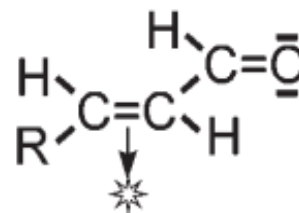
Mechanism: Surface adsorp. models



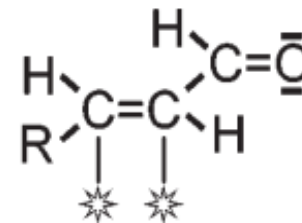
(A)
 $\eta^2\text{-(C,O): } \pi$



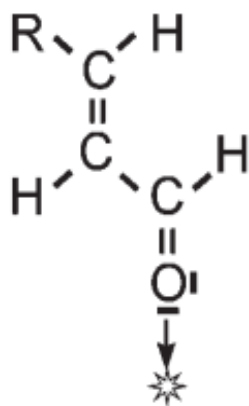
(B)
 $\eta^2\text{-(C,O): di-}\sigma$



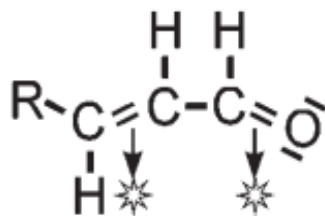
(C)
 $\eta^2\text{-(C,C): } \pi$



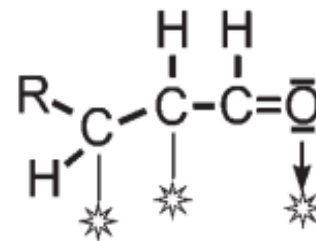
(D)
 $\eta^2\text{-(C,C): di-}\sigma$



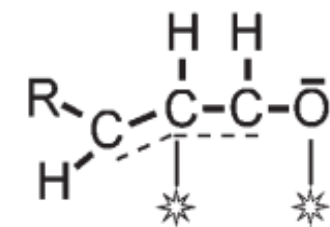
(E)
 $\eta^1\text{-(O): end-on}$



(F)
 $\eta^2\text{-(C,C) + } \eta^2\text{-(C,O): di-}\pi$



(G)
 $\eta^2\text{-(C,C) + } \eta^1\text{-(O)}$



(H)
 $\eta^4\text{-(C,C,C,O)}$

Different adsorption & activation sites on Catalysts

Why Ni-based Catalysis?

Cu-based catalysts: supported on Al_2O_3 , ZrO_2 , CeO_2 and TiO_2 etc. Peculiarly, Cu- Cr_2O_3 was the 1st established commercial process worldwide, by Davy Process (JM).

Ni-based: new type and have been commercialized recently.

Noble metals: mainly applied as co-catalysts

Hydrogenation activity of C=C bonds follows the order below:



Issues of catalysts

- **Toxicity**
- **Activity & Deactivation:** gas phase **peculiarly**
- **Porosity:** boiling & diffusion & heat transfer
- **Cost:** active site dispersion and amount
- **Mechanism:** Acid/Redox catalysis, Al_2O_3 , SiO_2 , CeO_2 , TiO_2 , ZrO_2 , etc:

Why CeO_2 is may improve the activity? (our work)

Support effects

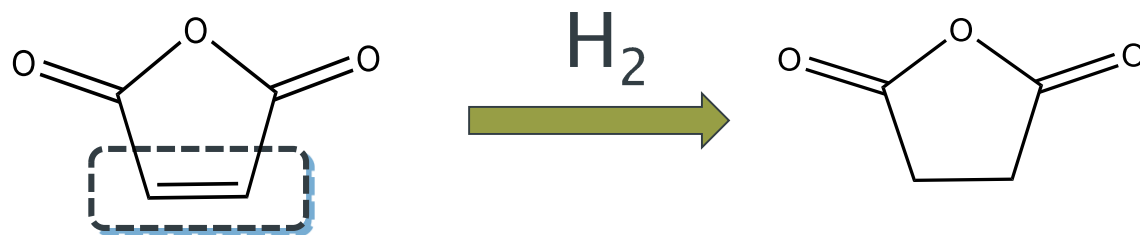
- ❖ **Acidity:** acid favors c-c double bonds Hydrogenation.
- ❖ **Redox property:** facilitate hydrogen spillover
- ❖ **Surface textures:** morphology & Porosity

Our thoughts and Solutions:

**Apply active support and improve Ni dispersion
&
Investigate the working mechanism behind**

Which bond is of MAH priority?

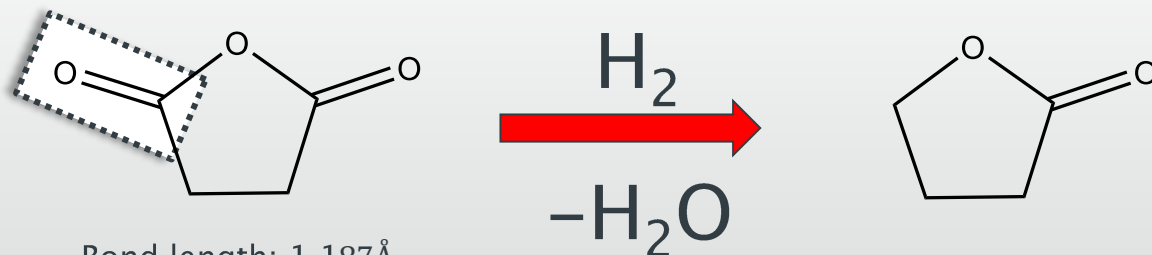
Simulation using Gaussian
C=C hydrogenation



Quicker
processes

Bond length: 1.346Å

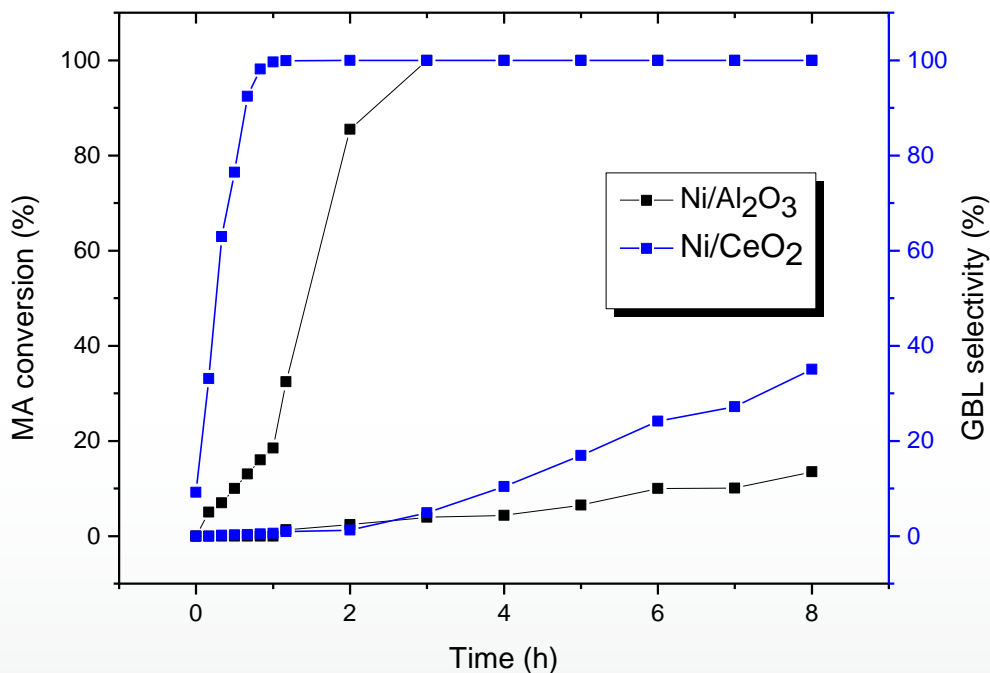
C=O (carbonyl) hydrogenolysis



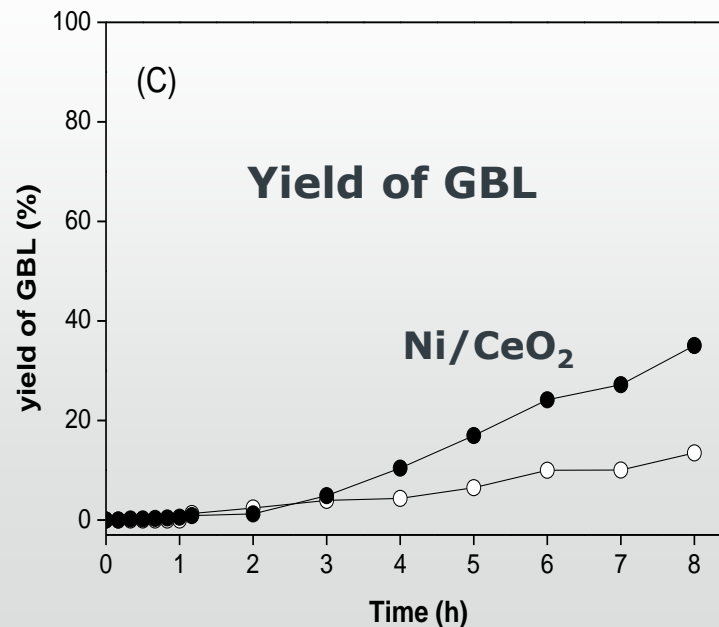
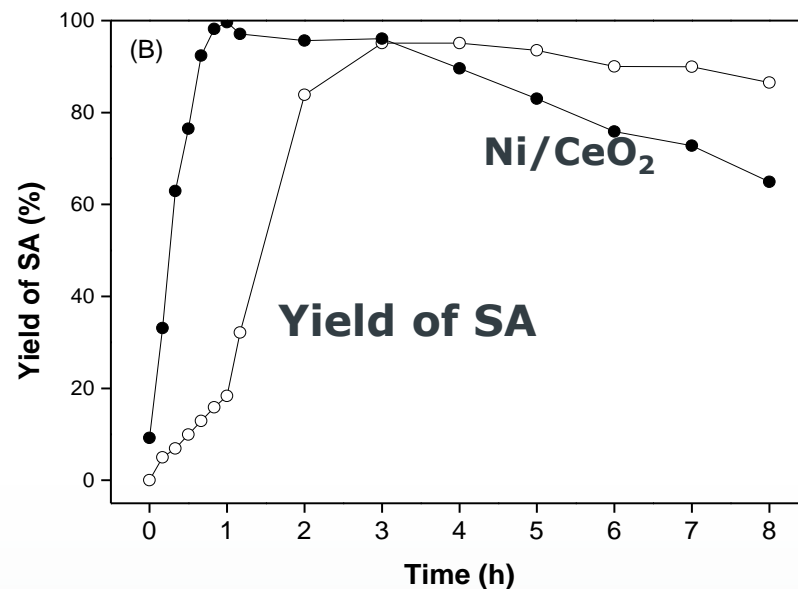
Bond length: 1.187Å

Higher
Ea

2. Active support effects

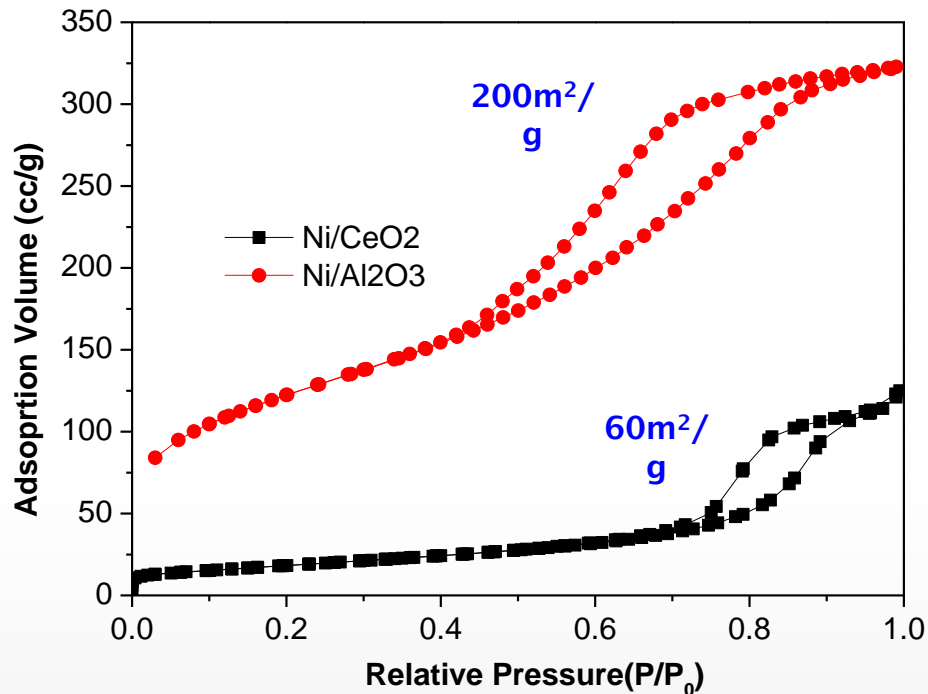


The conversion of MA over Ni/CeO₂ (solid circle) and Ni/Al₂O₃ (open circles) catalysts at 210 °C under 5 MPa for 8 h duration.

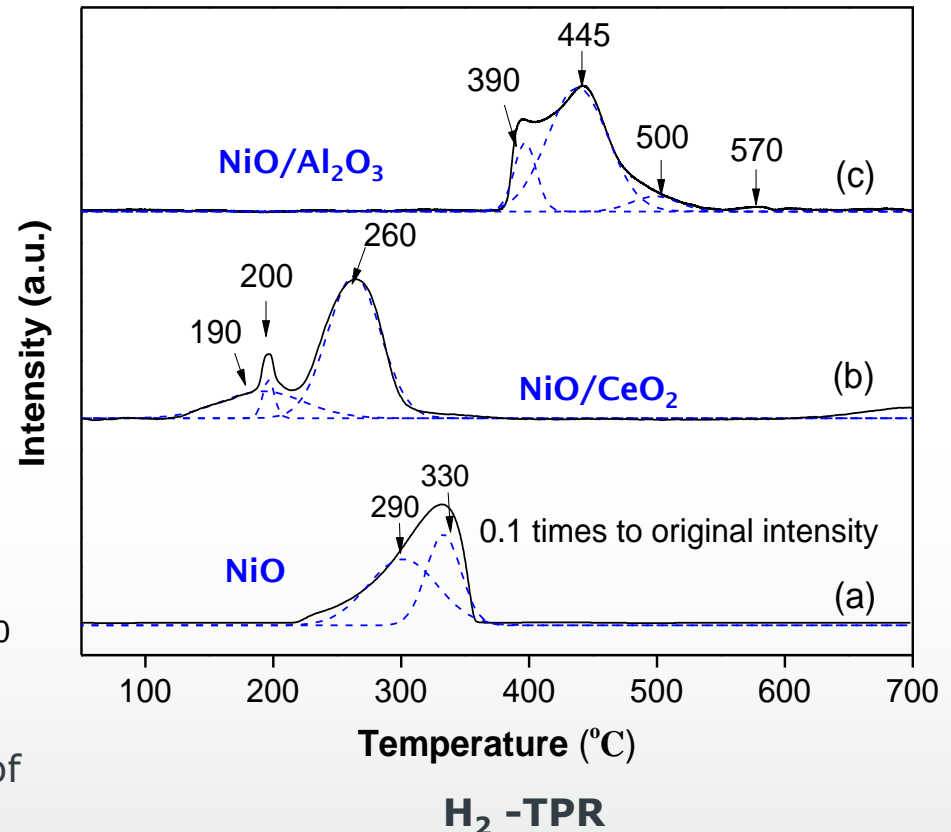


TOF of MA (~2.5 times):
0.49 mol/s on Ni/CeO₂;
0.2mol/s on Ni/Al₂O₃

Nano-size effects? More



N₂ adsorption-desorption isotherms patterns of Ni/CeO₂ and Ni/Al₂O₃

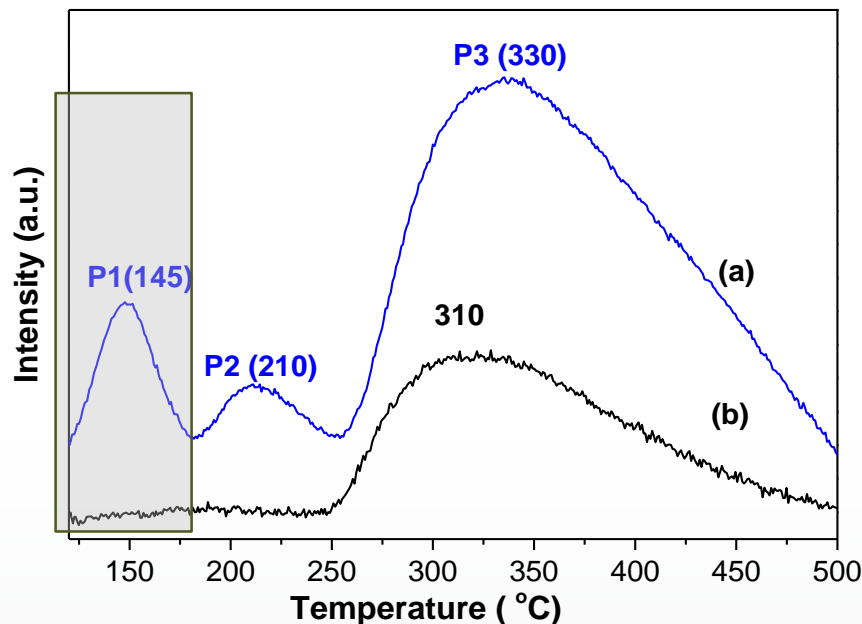


NiO Reduction temperature on CeO₂ is much lower than that on Al₂O₃. **WHY?** smaller particle size?

Crystallite size of Ni: 12.2nm for Ni/CeO₂; 16.5nm/Al₂O₃

H₂-Uptake analysis

H₂-TPD profiles of the Ni/CeO₂ (a) and Ni/Al₂O₃ (b) catalysts

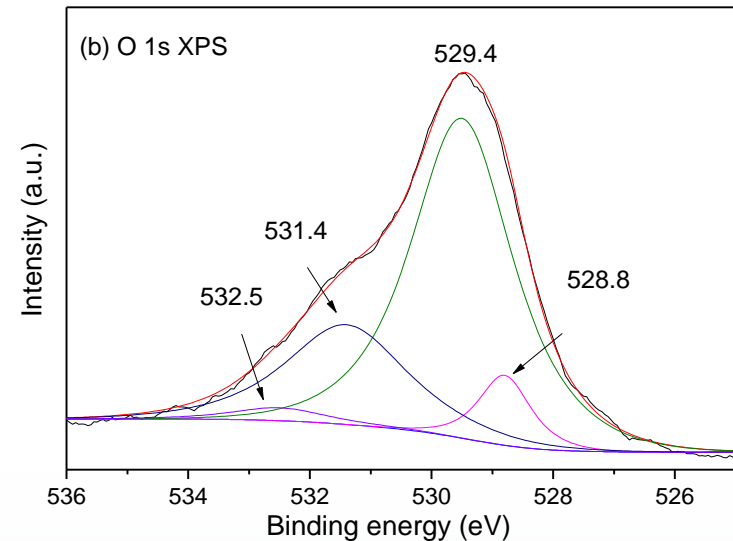
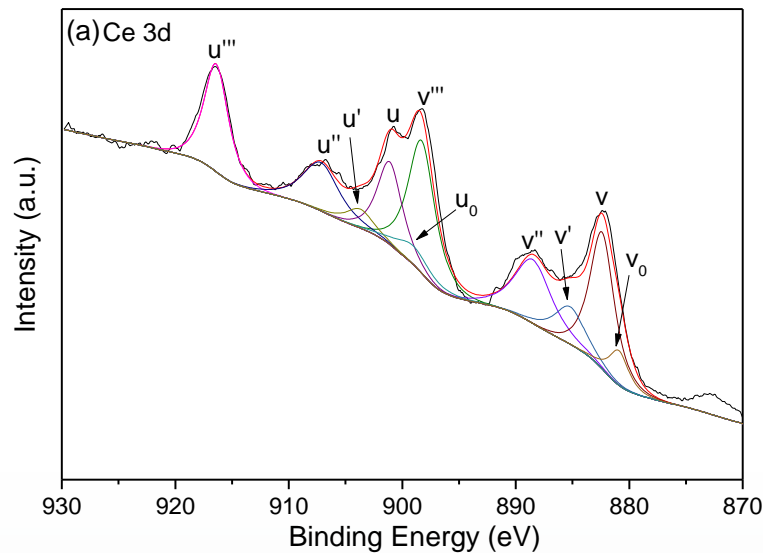


sample	n(H) ^a (μmol H ₂ /g cat)	n(H') ^b (μmol H ₂ /g cat)	n(H'') ^c (μmol H ₂ /g cat)	n(Ni _{surf}) ^d (μmol)	Ni dispersion (D) ^e (%)
Ni/CeO ₂	0.75	0.37	9.26	2.08	1.22
Ni/Al ₂ O ₃	-	-	4.97	0.99	0.58

H₂ chemisorption capability of the reduced samples

^{a,b,c} n(H), n(H'), and n(H'') represent the amount of H₂ desorbed at 145, 210 and ca. 310–330 °C, respectively. ^d n(Ni_{surf}) represents the amount of surface-exposed Ni on the catalysts, assuming H/Ni=1 and Ni=2*(H₂ desorption amount). ^e Ni dispersion =(Ni_{surf}/Ni_{total}), Ni_{total} means the total amount of Ni in the catalysts.

Quantitative analysis of O_{vac}



The core-level XPS spectra of the reduced Ni/CeO₂ catalyst (a) Ce 3d (a) and O1s (b)

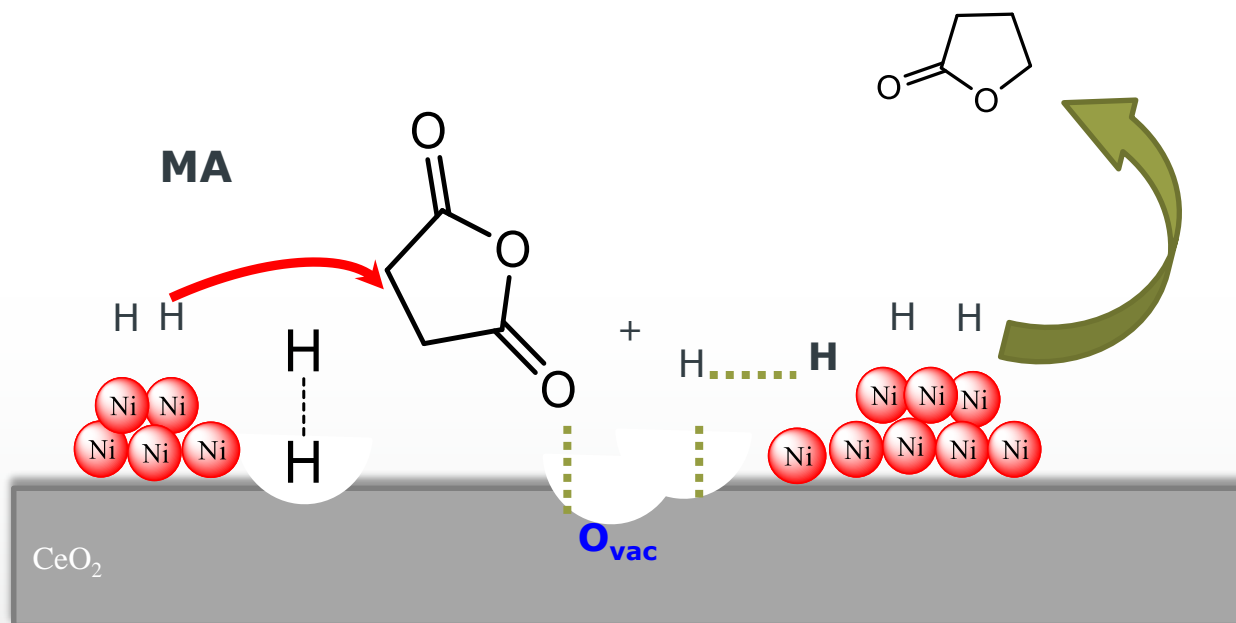
$$[Ce^{3+}] = \frac{[Ce^{3+}]}{[Ce^{3+}] + [Ce^{4+}]} = \frac{u' + v' + u_0 + v_0}{u''' + v''' + u'' + v'' + u + v + u' + v' + u_0 + v_0} = \frac{3114.2}{19686.9}$$

$$x = \frac{[O]}{[Ce^{3+}] + [Ce^{4+}]} = \frac{3}{2} \times [Ce^{3+}] + 2 \times [Ce^{4+}] = 1.88$$

Experimental $[O] = 1.77$

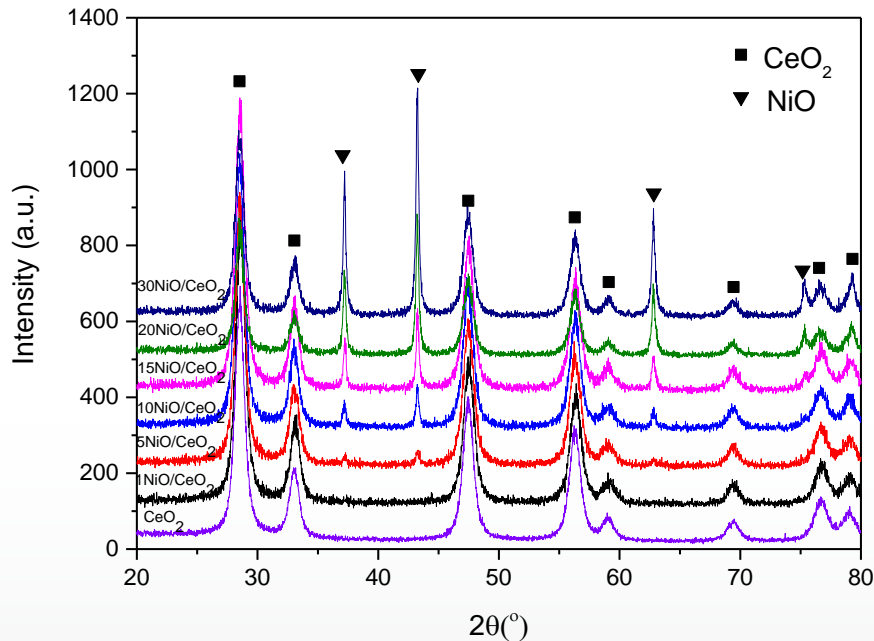
oxygen vacancy was estimated as $\sim 5.9\%$

Synergism of PS & Ovac

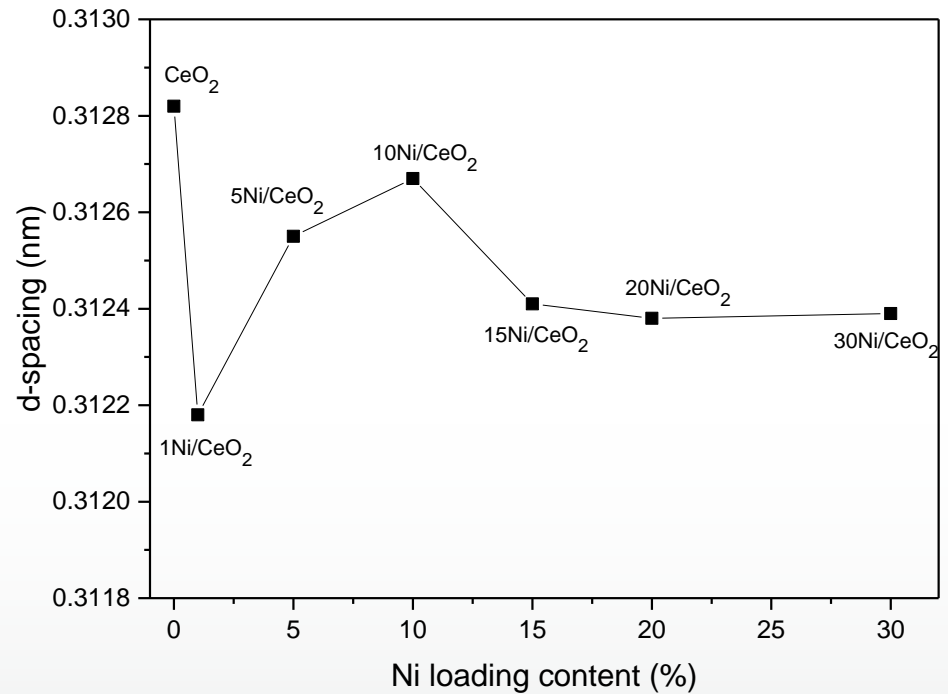


We attributed this phenomena to the synergistic effect of PS & O_{vac}

3. Effects of Ni Loading



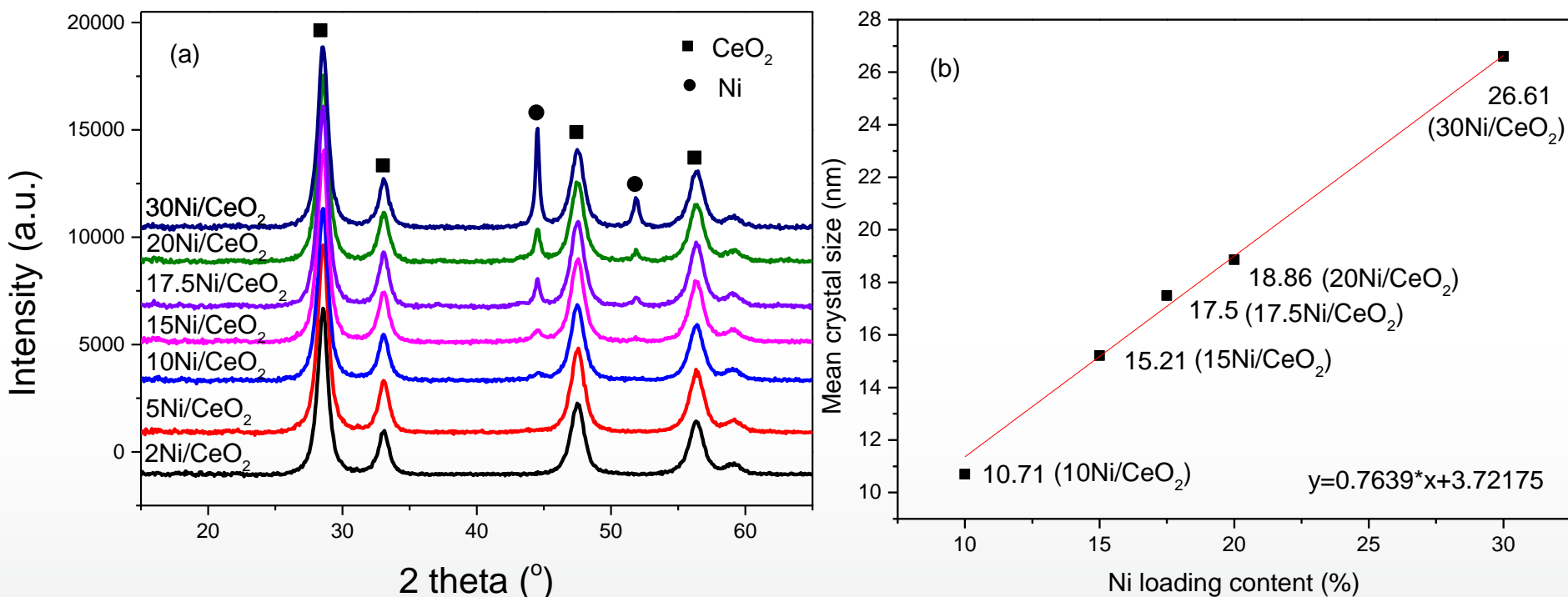
NiO diffraction patterns enhanced as increasing [Ni]



d-spacing of CeO_2 (111) decrease as Ni incorporate into the matrix of CeO_2 , due to the radius of Ni^{2+} (0.070 nm) is smaller than Ce^{4+} (0.087 nm).

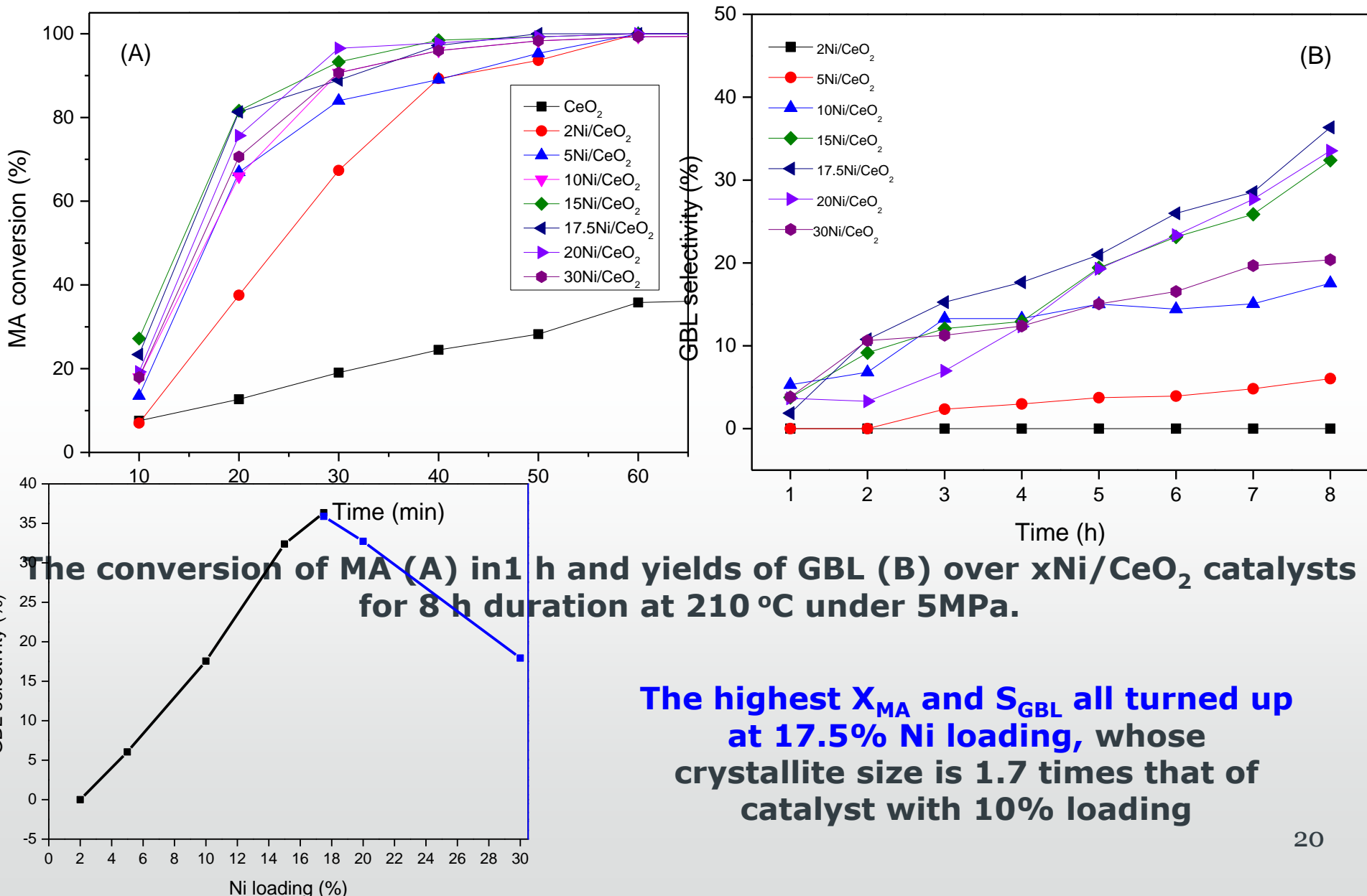
As [Ni] increased from 1 % to 10 %, the d-spacing of CeO_2 reduced from 10 % to 30 % is not clear, however, **Ce^{4+} ions were reduced to Ce^{3+} .**

Particle Size is really not all

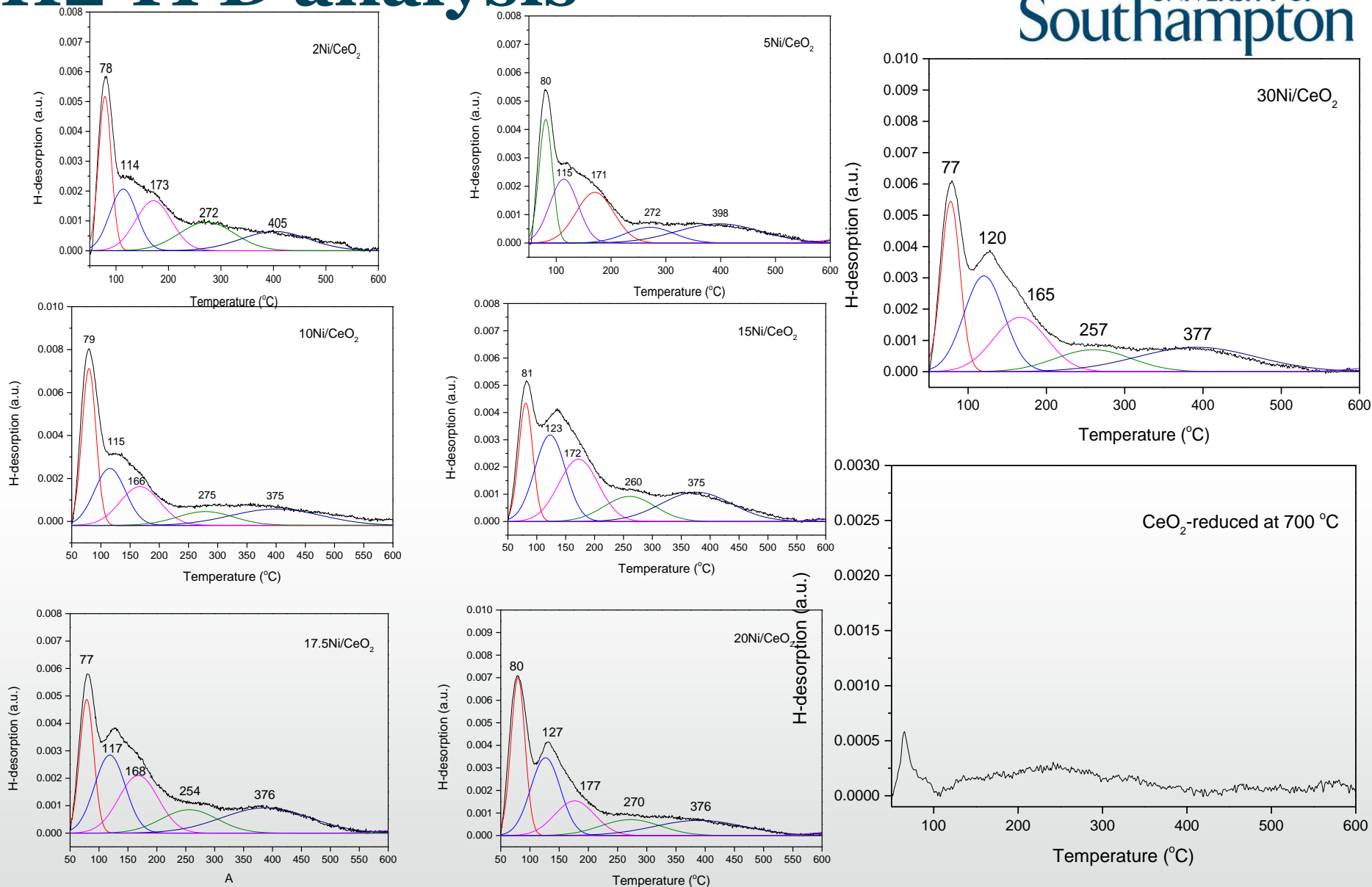


(a) XRD pattern of $x\text{Ni}/\text{CeO}_2$ catalysts and (b) Ni crystallite size **vs** Ni loading

Ni Loading effects on MAH

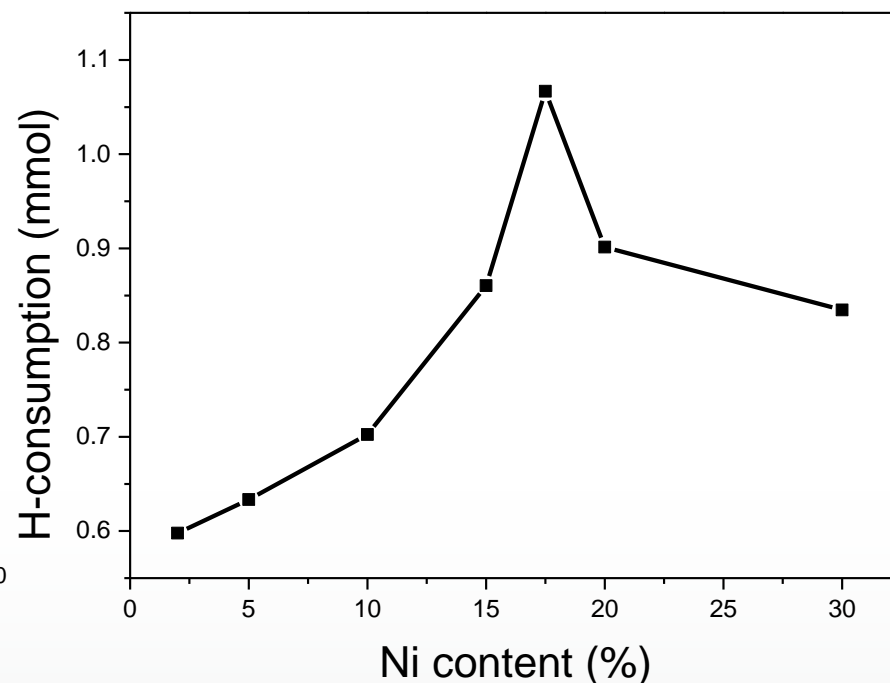
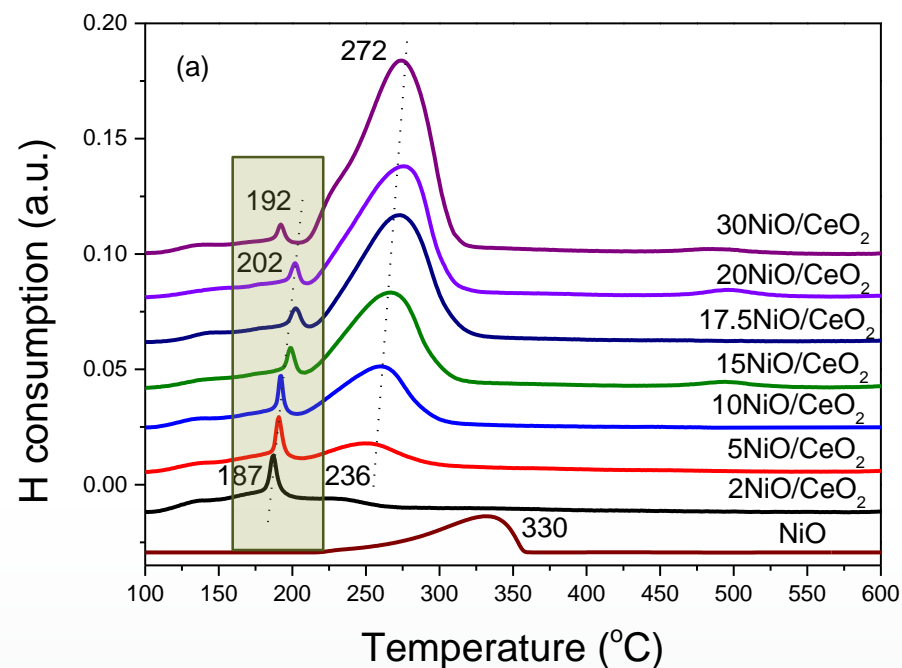


H₂ TPD analysis



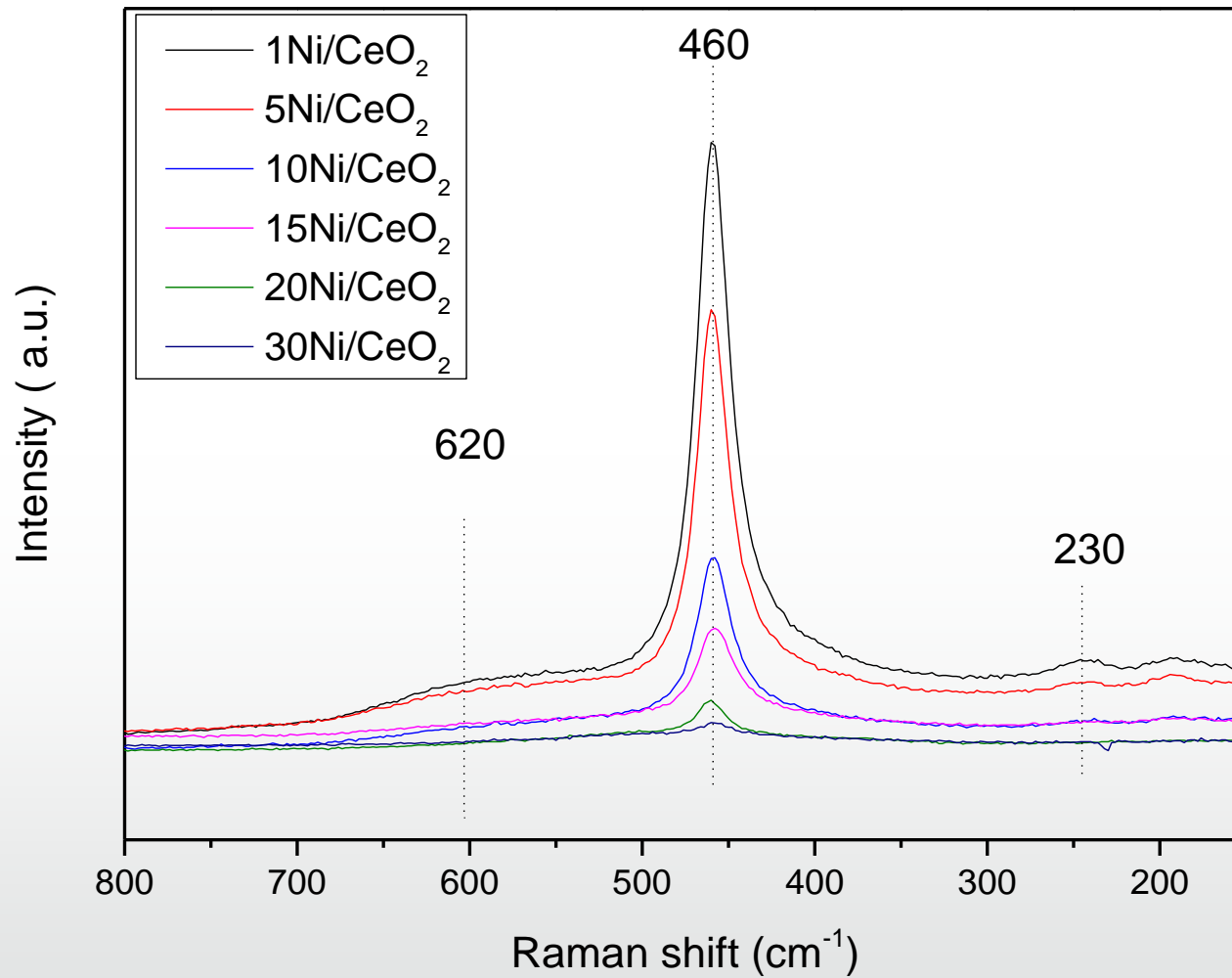
H-TPD profiles of the xNi/CeO₂ catalysts and reduced CeO₂

O_{vac} is easier to create

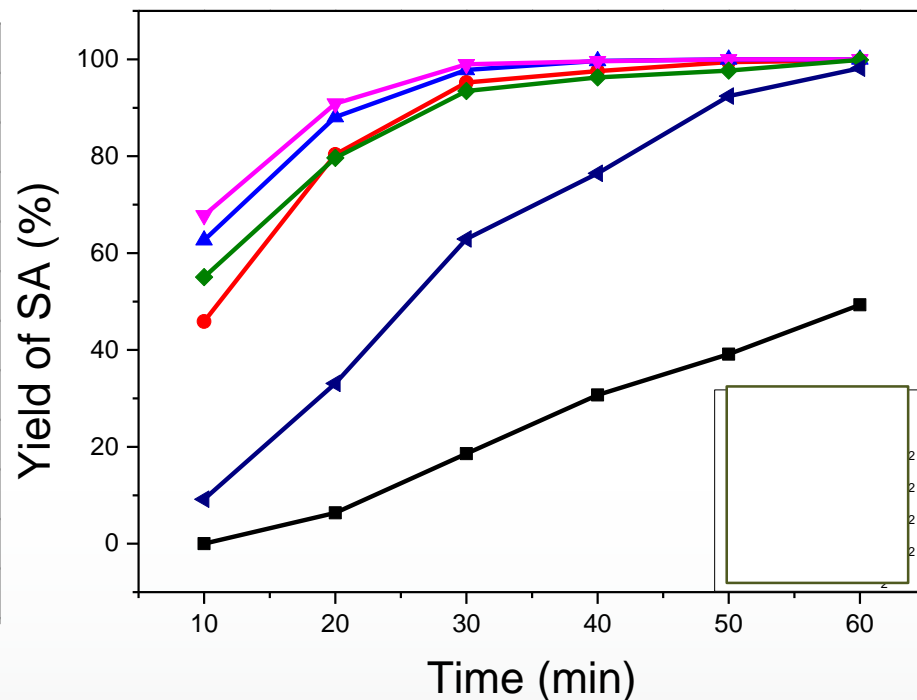
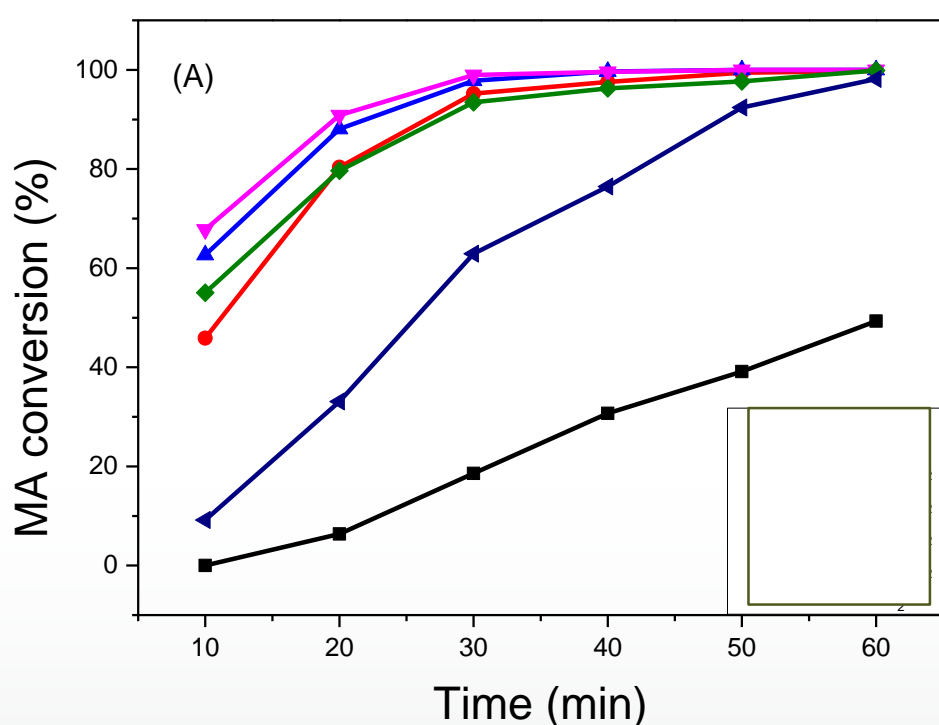


(a) TPR profiles of $x\text{Ni}/\text{CeO}_2$ catalysts and (b) plot of H_2 consumption for support to create the oxygen vacancies versus Ni loading content

How/Why it is active?



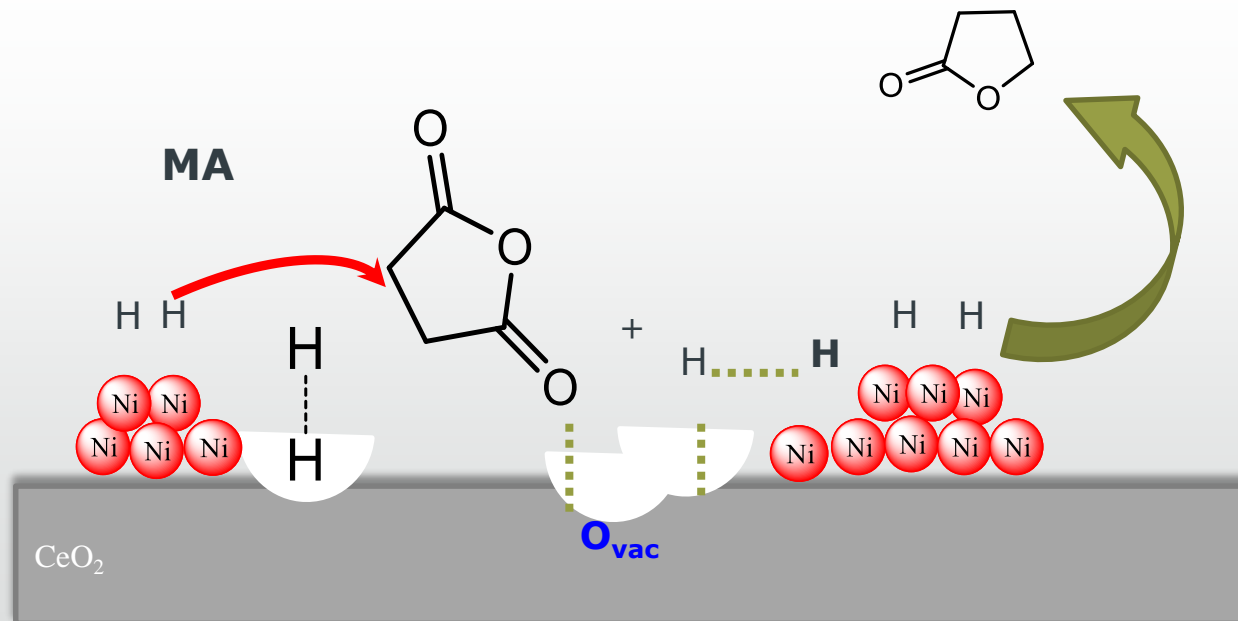
3. Modifying to improve



MA conversion (A) and SA yield (B) on modified Ni-based catalysts (210 °C under 5 MPa for 1 h duration)

Conclusion

- Ni/CeO₂ may be a novel and environment friendly catalyst for MAH where O_{vac} of CeO₂ plays profound roles
- Their performance depends on the Ni loading and O_{vac} amount
- The further modification of CeO₂ have further confirmed O_{vac} function that consolidated our new MAH mechanism



Acknowledgement

UNIVERSITY OF
Southampton



Sir John Houghton



Lord John Krebs



Prof. Peter P. Edwards, FRS



Prof. Martyn Hill



Prof. Mark Crocker



Prof. Jinghai Li



Prof. Yongxiang Zhao

Mr. Xin Liao



Prof. Peter Dobson



Dr. Martin Jones



Jesus College



SHELL
FOUNDATION



The Royal Academy
of Engineering

Thanks!