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Chemical Catalysis for Bioenergy

Methyl Ketone Condensation over Tailored Metal Oxides

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Presented by: Derek Vardon, PhD
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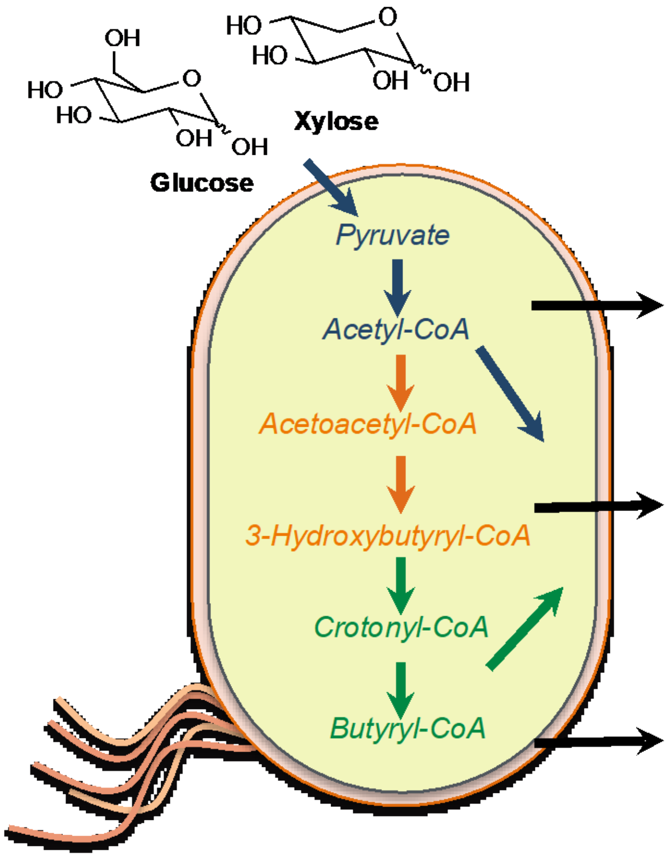
Presentation Outline

1) Evaluating tailored MgO nano-catalysts

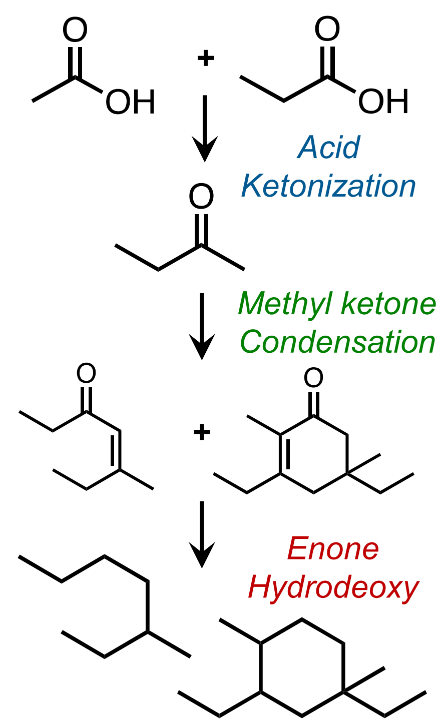
2) Determining active surface and mechanism

3) Assessing the impact of water exposure

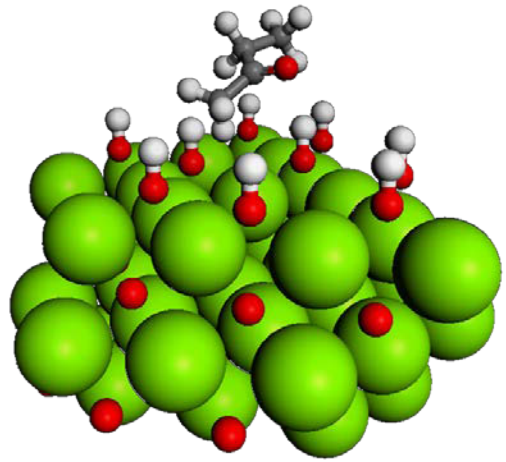
Why methyl ketone condensation?



Biojet Hydrocarbons



Tailored Metal Oxides

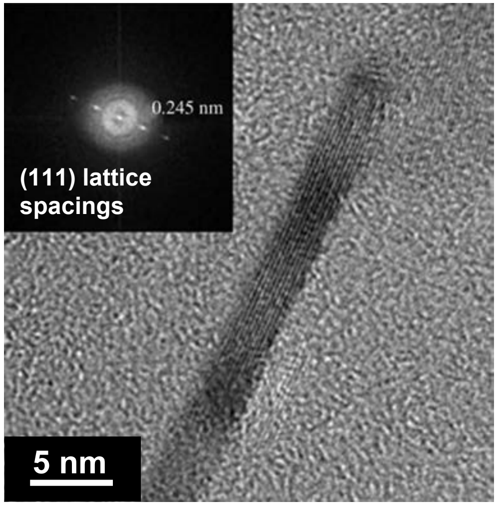


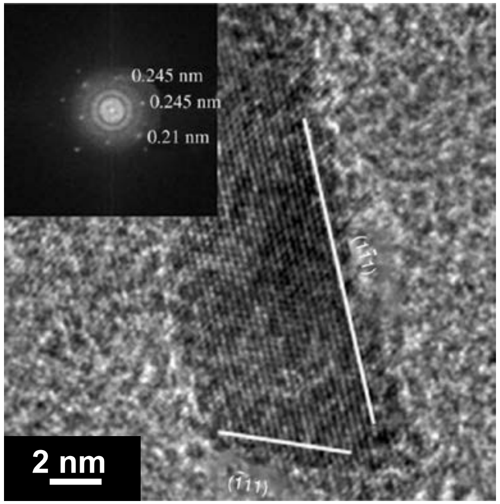
Evaluate MgO basic catalysts for their activity and stability under catalytically relevant conditions

Methyl ketones can be catalytically upgraded to cycloparaffins for low-sooting aviation fuels

Sacia (2015) ChemSusChem. 8, 1726-1736

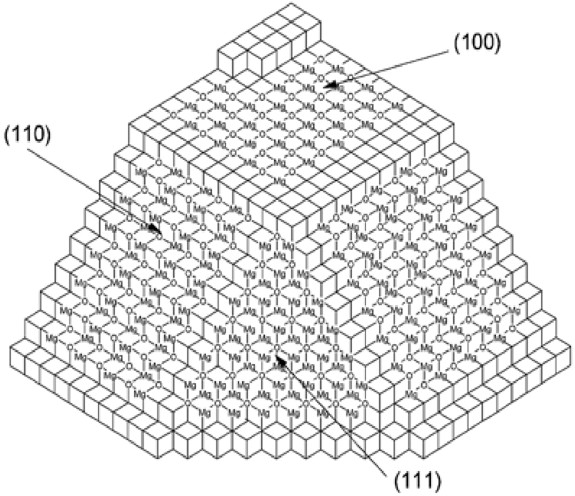
Why tailored MgO basic catalysts?



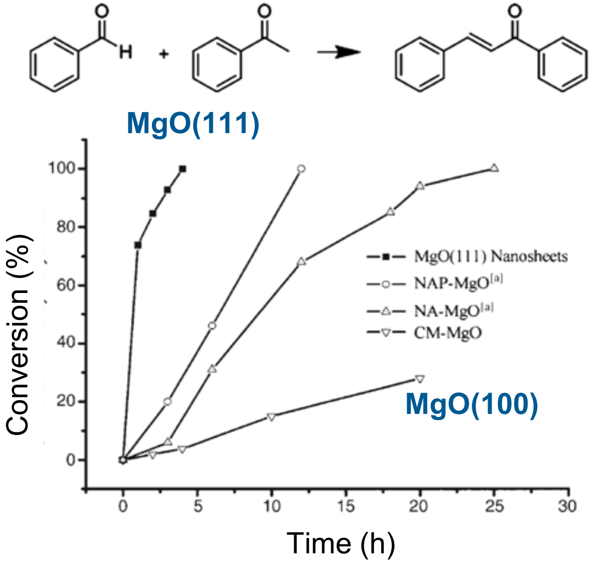


Tailor MgO nanoparticle morphology for high surface area and increased mass normalized activity

Expose select surface facets for M-O coordination state that directly impacts reactivity



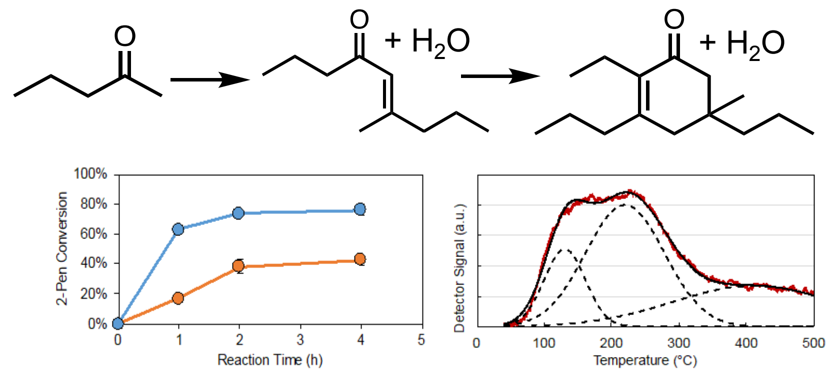
Claisen-Schmidt Condensation

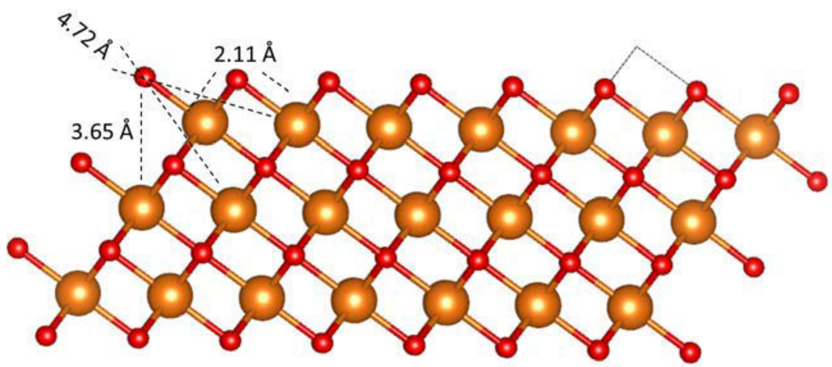


[c] Zhou (2006) Angewandte. 188, 7435-7439

Remaining research challenges

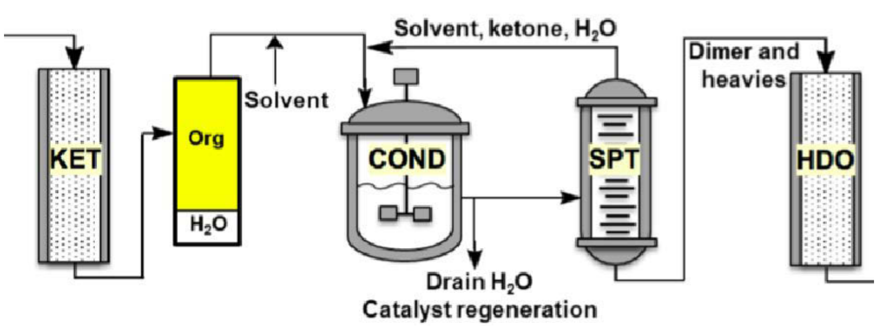
Synthesize tailored MgO catalysts and compare initial activity for methyl ketone condensation





Assess the working MgO catalytic surface and associated reaction mechanism

Determine surface and morphological stability with continuous water exposure

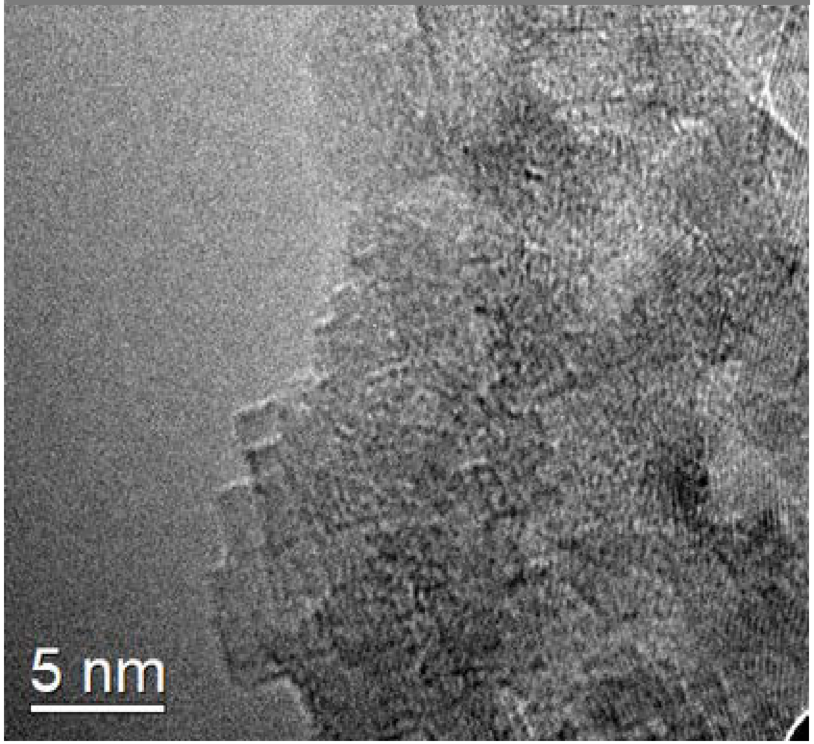


Part 2

Evaluating reactivity and working catalytic surface for ketone condensation

Synthesis of nano-MgO catalysts

MgO(111) Nanosheets



Ryan Richards Group

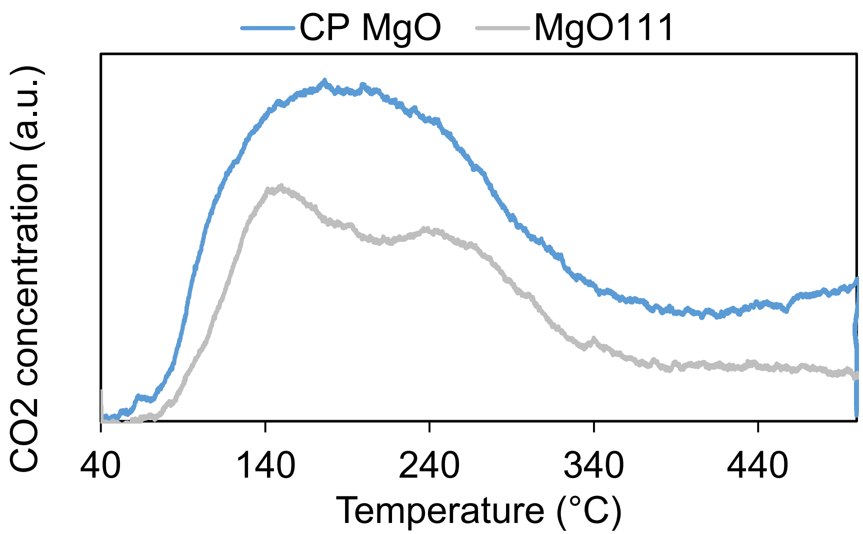
Property	CP Nano MgO(100) [a b]	Nanosheet MgO(111) [c]
Synthesis Method	water addition thermal anneal	R-OH addition thermal anneal
Morphology/ Dimensions	100-300 nm particles	5 x 200 nm sheets
Surface area ($m^2\ g^{-1}$)	143	181

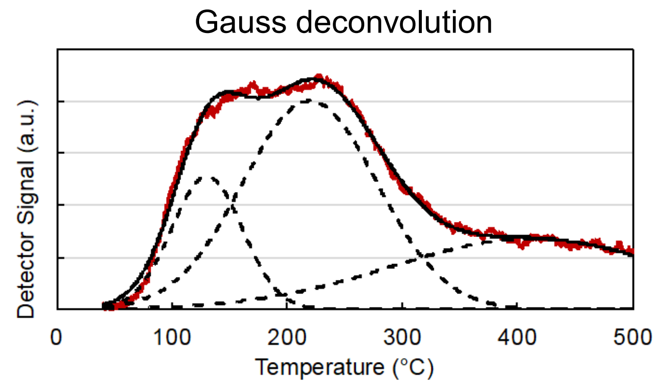
Pretreatment Conditions: 500°C under flowing inert for 6h

Prepared MgO nanomaterials with comparable surface area to evaluate impact of (111) vs (100) surface facet

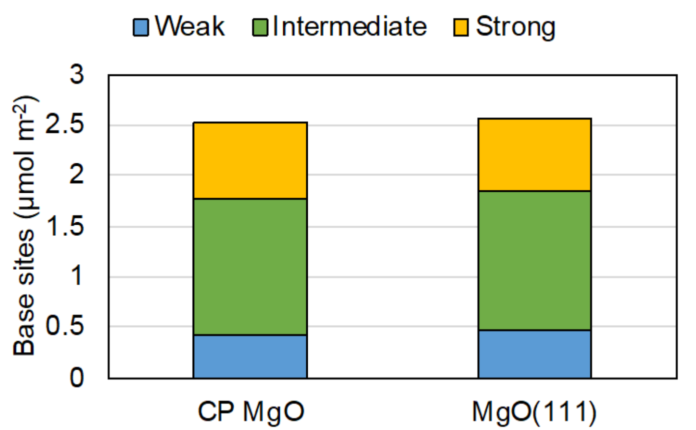
[a] Choudary (2004) JACS. 126, 3396-3397 [b] Koper (1997) Chem Mat. 9, 2468-2480 [c] Zhou (2006) Angewandte. 188, 7435-7439

Evaluating base sites by CO_2 TPD





CO_2 Base Sites	CP Nano MgO(100) [a]	Nanosheet MgO(111) [b]
Mass (μmol CO_2 g^{-1})	351	461
Area (μmol CO_2 m^2)	2.5	2.5



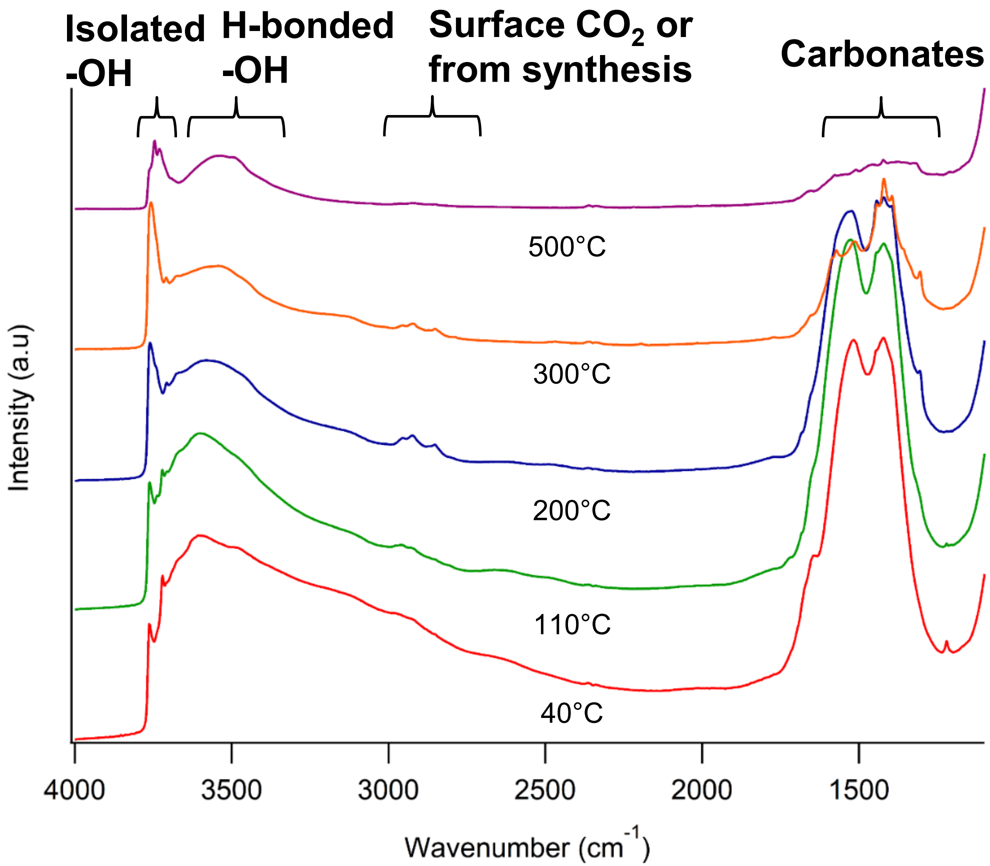
Pretreatment Conditions: 500°C under flowing inert for 6h

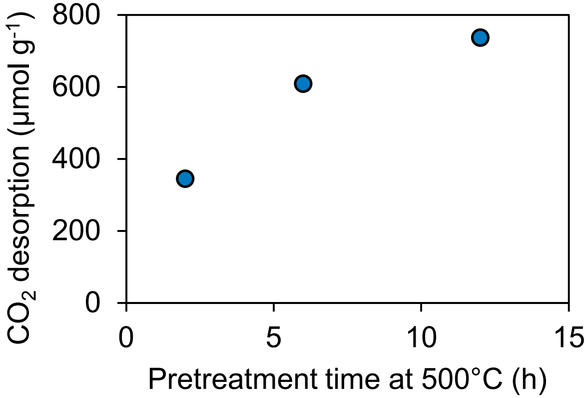
Area normalized base site quantity and distribution are comparable for both MgO catalysts up to 500°C

Cosimo et al. (2014) Catalysis. 26: 1-28.

Xiangchen Huo, Davis Conklin NREL

MgO(111) DRIFTS characterization





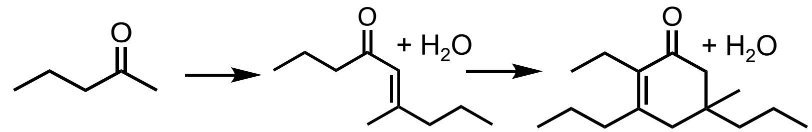
MgO(111) Pretreatment	Surface area (m^2 g^{-1})
No pretreatment	215
Static air 350°C, 4h	184 (-14%)
Static air 500°C, 4h	123 (-43%)
Flowing inert 350°C, 4h	205 (-5%)
Flowing inert 500°C, 4h	185 (-14%)

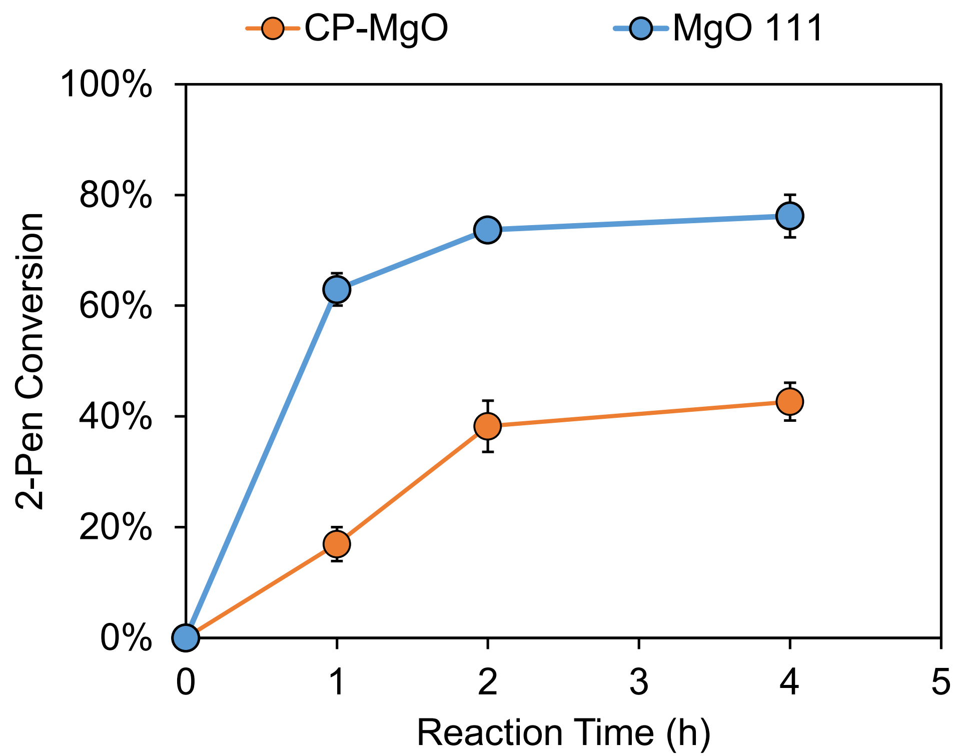
MgO(111) surface and morphology highly sensitive to pretreatment and environmental exposure

Mutch et al. (2018) JACS. 140, 4736-4742. Chowdary et al. (2018) NJC. 42, 14194-14202. *Xiangchen Huo, Davis Conklin NREL*

Initial ketone condensation activity

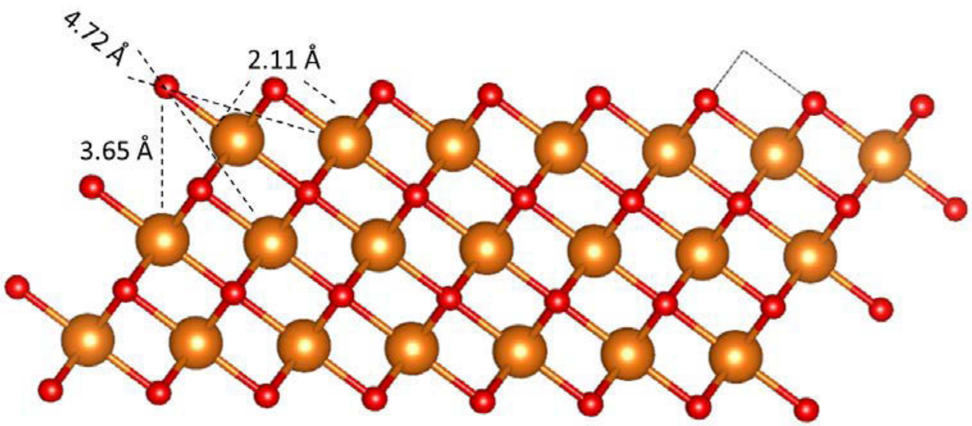
Rxn conditions: 20 mL of 0.01M 2-pentanone in toluene, catalyst loading for equivalent surface area, 150°C, inert atm, 800 rpm. Catalyst pretreated at 500°C inert 6h.





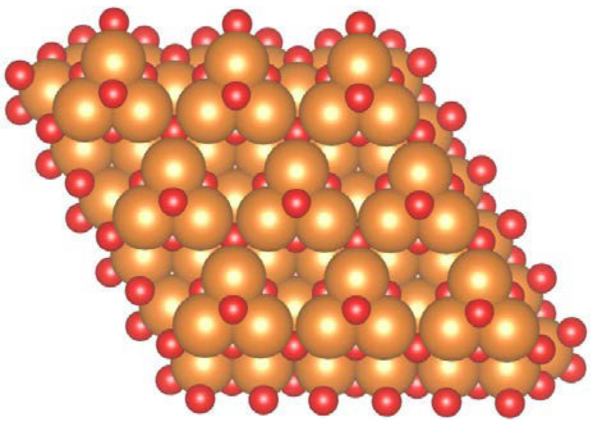
Batch reactor screening shows initial higher condensation activity with MgO(111) than MgO(100)

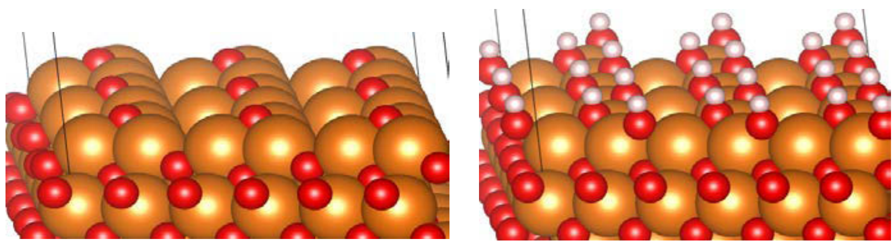
Surface termination for MgO(111)



Historically, MgO(111) proposed as alternating cation and anion layers with concerns of surface stability

Pal and Paly (2015) Nanoscale. 34, 14159-14190.

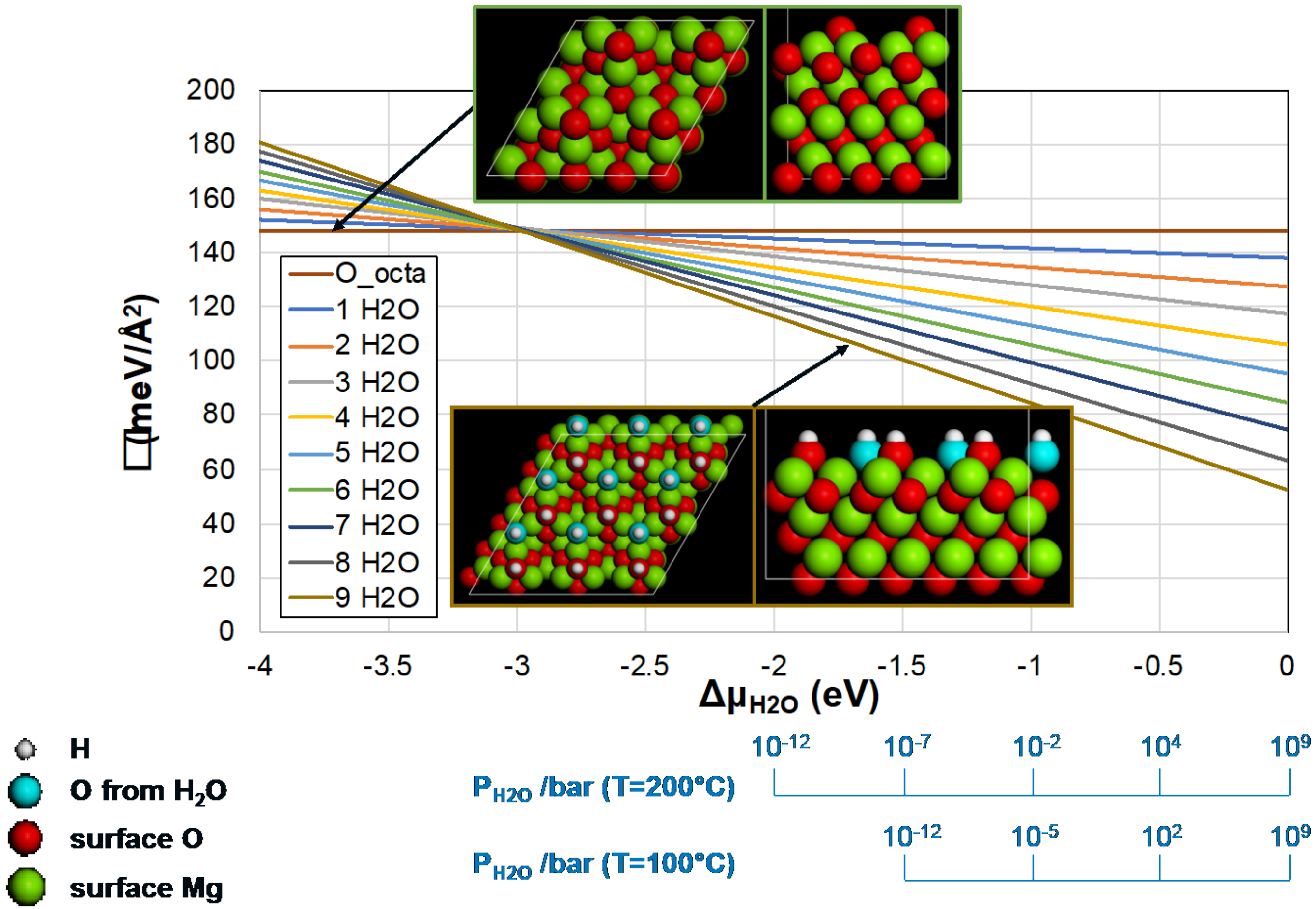




Recent experimental and computational efforts suggest MgO(111) octopolar surface termination may be the most stable

Bajdich (2015) Physical Reviews B. 91, 155401.

H_2O surface coverage for MgO(111)



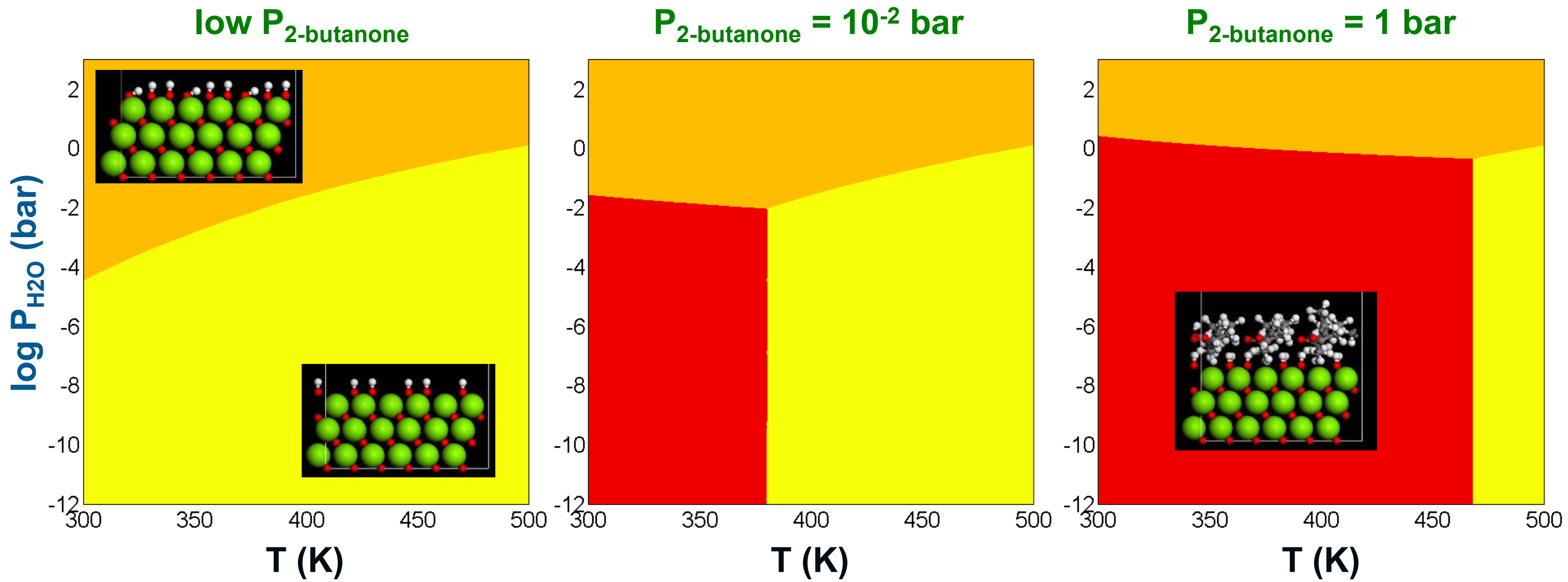
Even with low partial pressure of exposure, water readily dissociates to cover MgO(111) surface

Competitive adsorption on MgO(111)

MgO(111) surface coverage

- (yellow) dissociated H_2O (i.e. hydroxylated MgO(111))
- (orange) dissociated H_2O followed by physisorbed H_2O
- (red) dissociated H_2O followed by physisorbed 2-butanone

Increasing Ketone Pressure

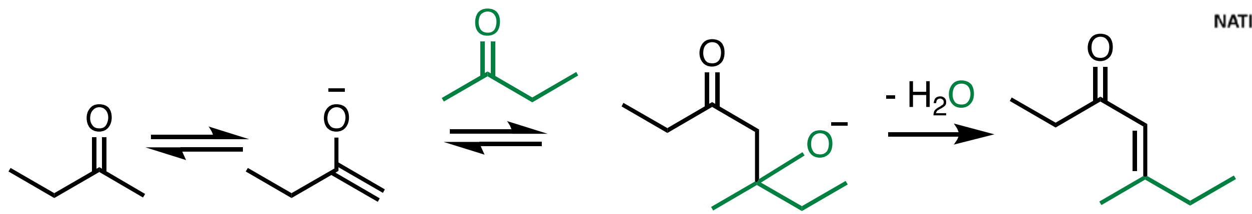


Likewise, even in the presence of ketones water dissociates to cover MgO(111) surface with hydroxyls

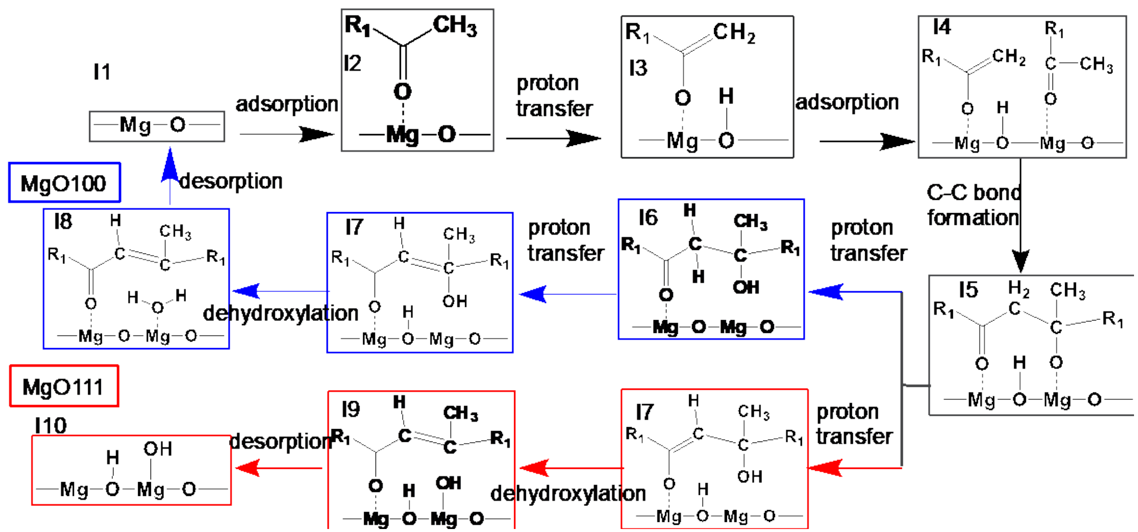
Ketone condensation rxn pathway

Argonne NATIONAL LABORATORY

Aldol Condensation Mechanism



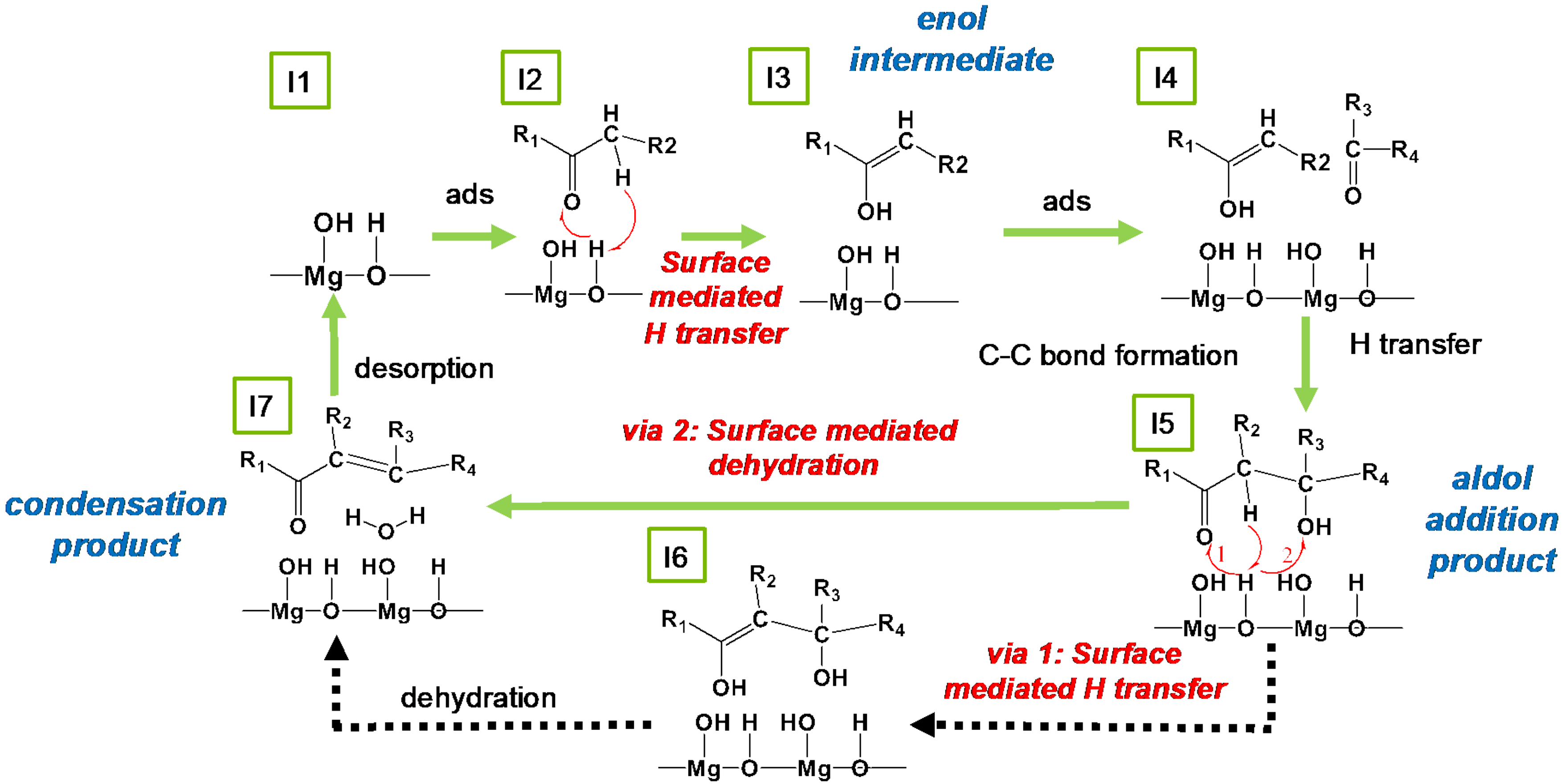
Surface Mediated Mechanism



Evaluate ketone condensation reaction mechanism on MgO(100) and MgO(111) surfaces

Mingxia Zhou, Rajeev Assary ANL

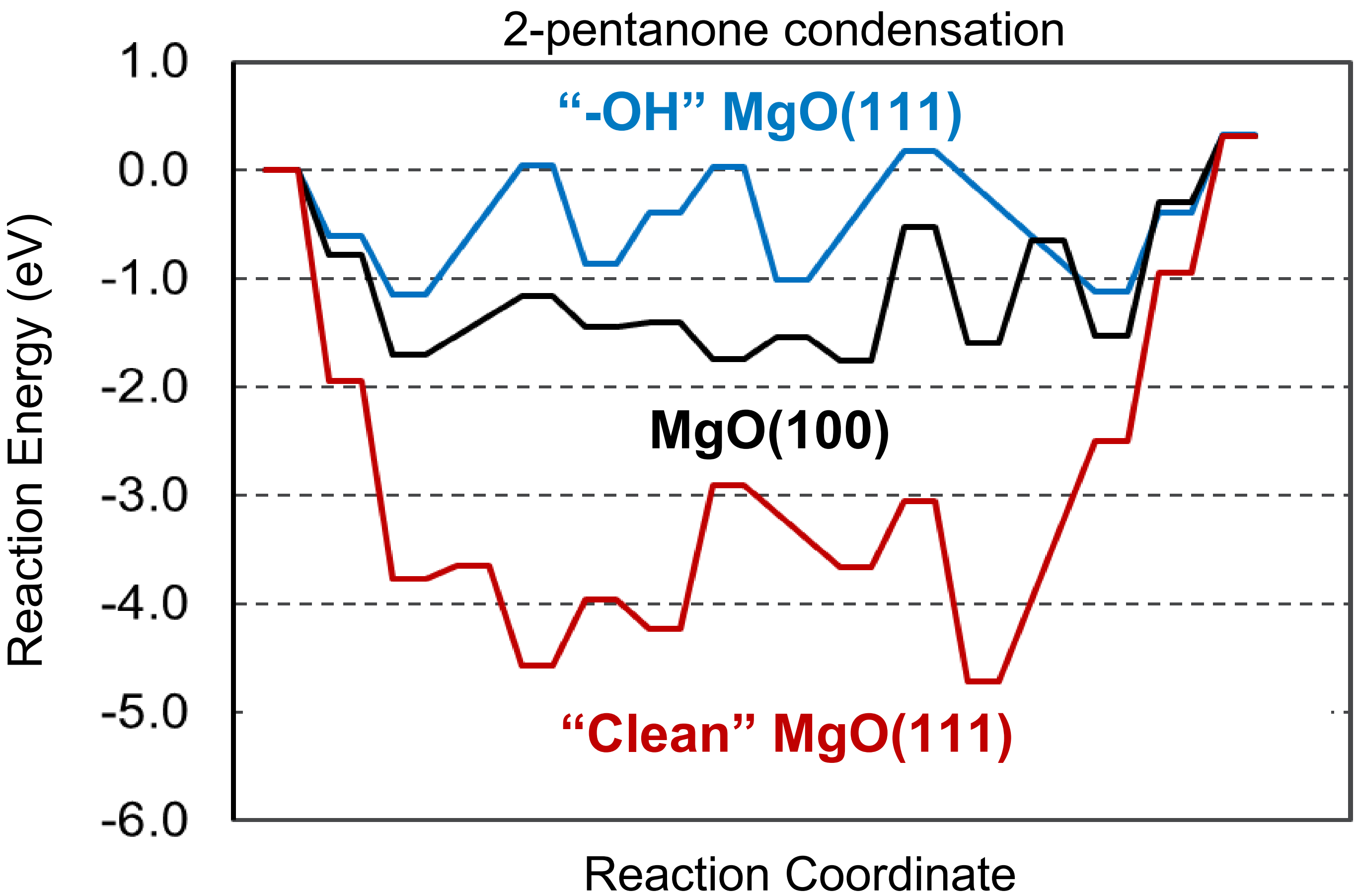
Role of surface –OH during reaction



Surface hydroxyl groups on MgO(111) may facilitate proton transfer to lower key transition states

Mingxia Zhou, Rajeev Assary ANL

Potential energy surface for COND



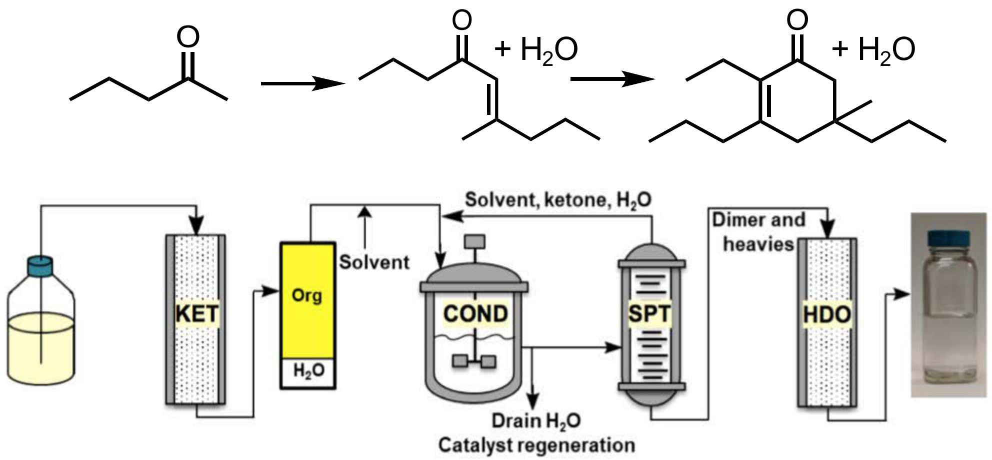
Intermediates would bind excessively strong on "clean" MgO(111), supporting "-OH" terminated surface

Mingxia Zhou, Rajeev Assary ANL

Part 3

Surface & morphological stability of MgO(111) with water exposure

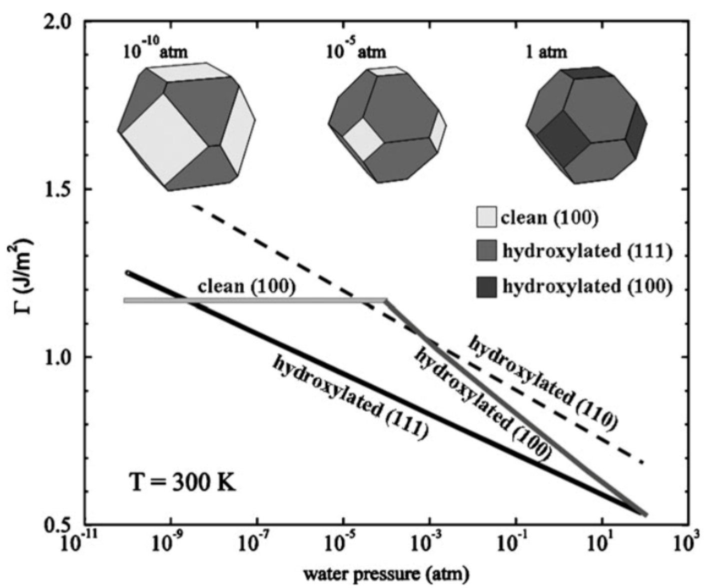
Continuous ketone condensation



Catalytic process needs to be *active, selective, and stable* with water generated *in situ* and likely present in the feed

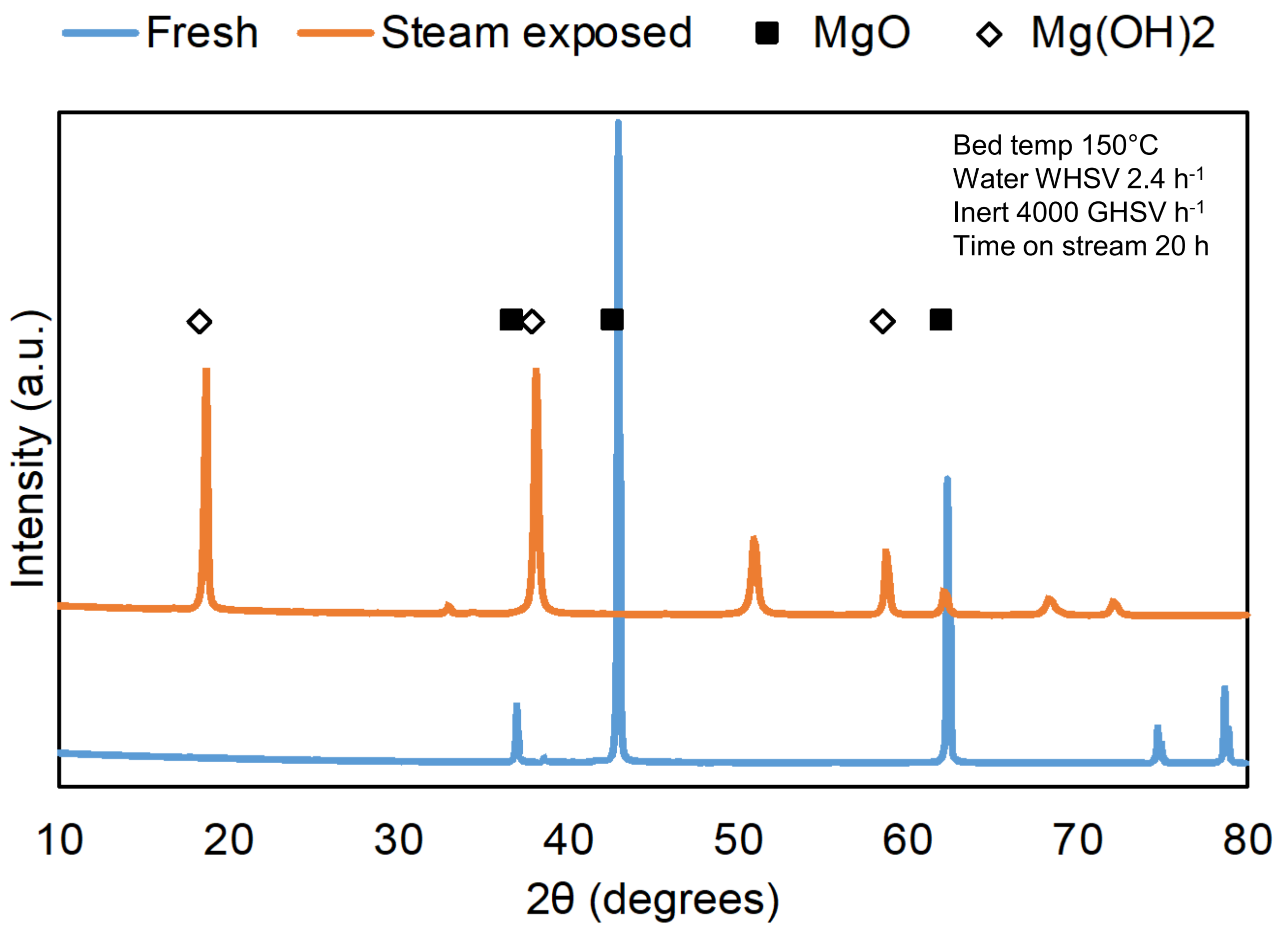
Scott (2018) ACS Catalysis. 8, 8597-8599

For tailored nano-metal oxides, facet stability and particle morphology remain relatively underexplored with catalytically relevant conditions

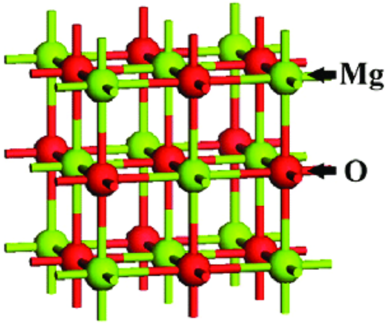


Geysermans (2009) Phys Chem Chem Phys

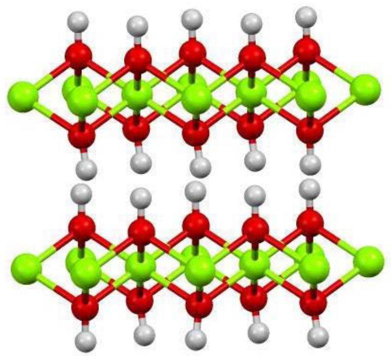
Bulk restructuring to form $Mg(OH)_2$



MgO(100)



$Mg(OH)_2$

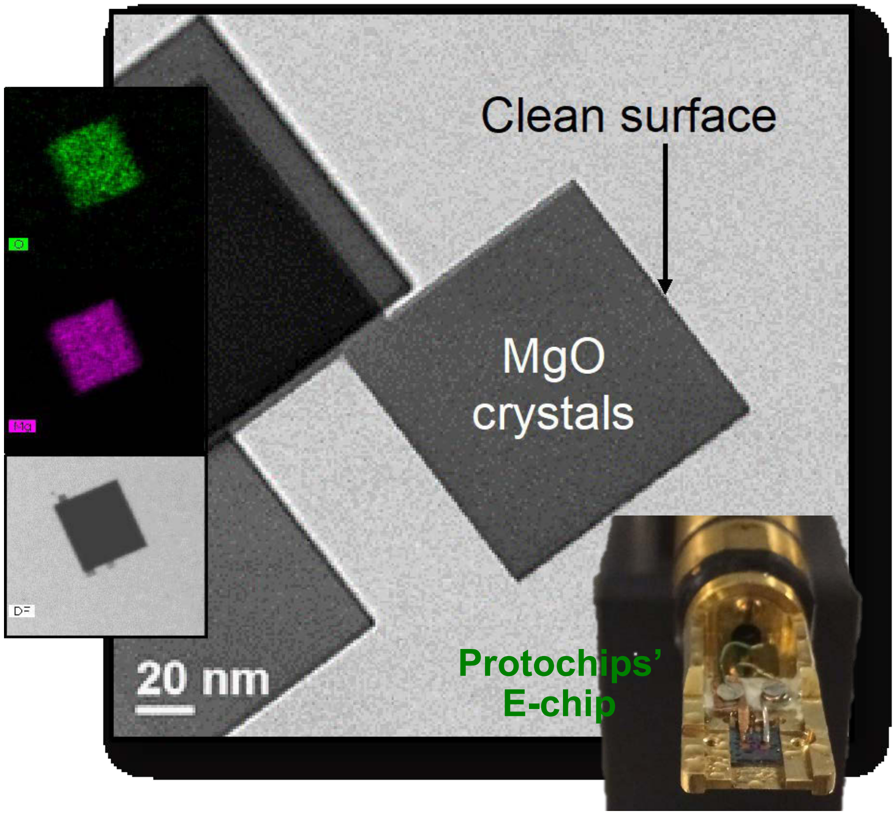


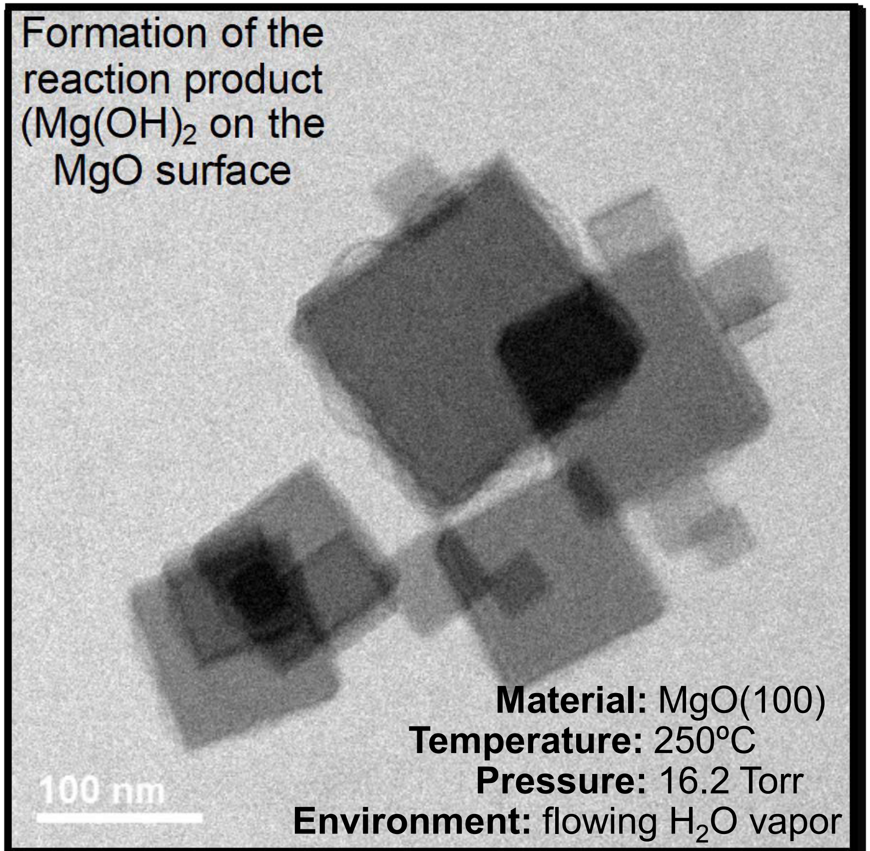
Preliminary steam exposure tests on MgO(100) powder show dramatic restructuring of bulk to form $Mg(OH)_2$

Xiangchen Huo, Davis Conklin NREL

MgO(100) *in situ* TEM H_2O exposure

Oak Ridge National Laboratory

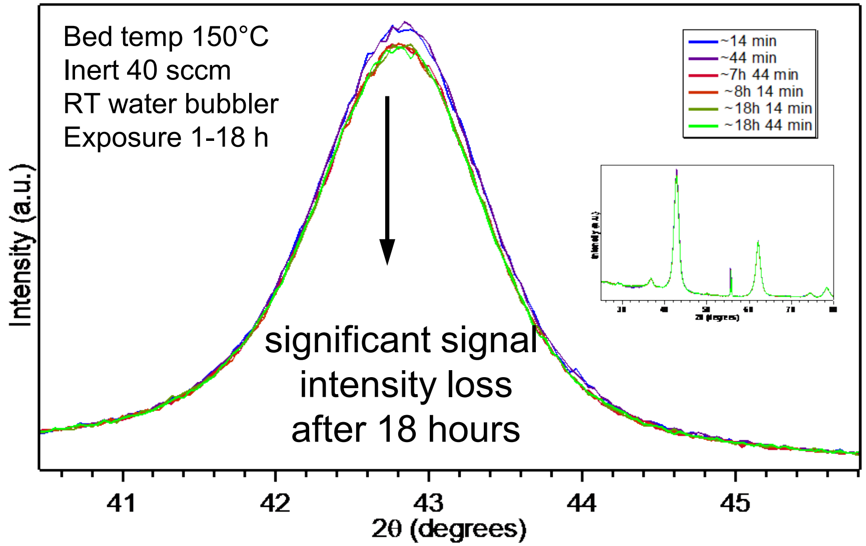




Low levels of water exposure can result in amorphous $Mg(OH)_2$ with MgO(100) nano-cubes

Unocic (2019) Microscopy and Microanalysis. Submitted.

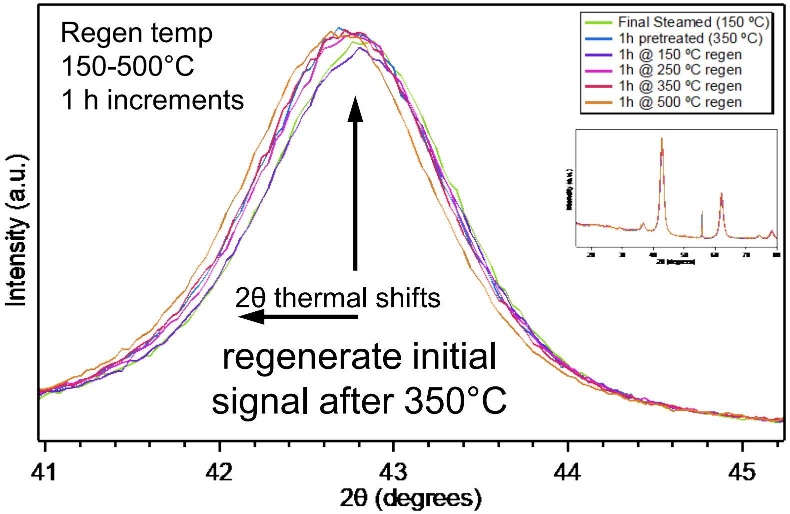
MgO(111) *in situ* XRD with steam



N_2 + H_2O atm (40 sccm through RT bubbler)

With steam exposure, MgO(111) experiences loss of signal intensity, indicative of restructuring

With thermal regeneration, MgO(111) XRD signal returns to initial "fresh" state after heating to 350°C

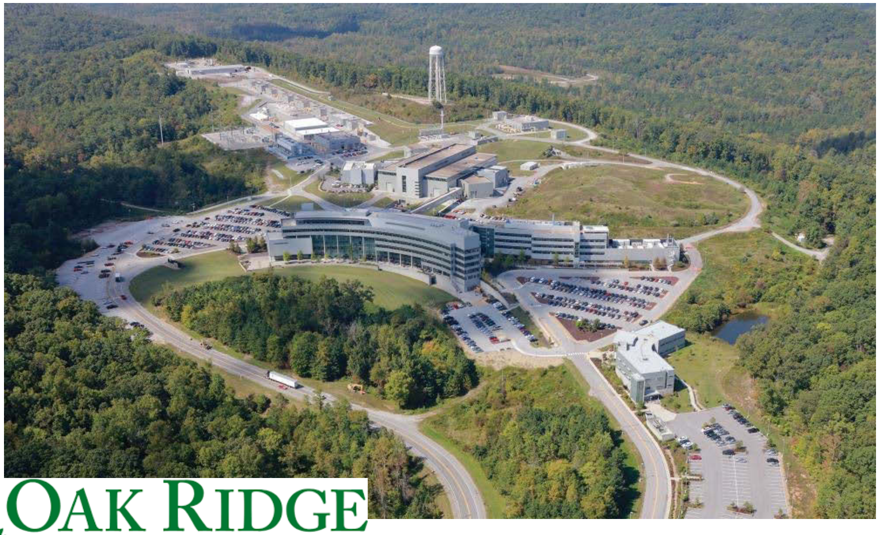


Heat sample in 1 hour increments from 150-500°C

Fred Baddour NREL

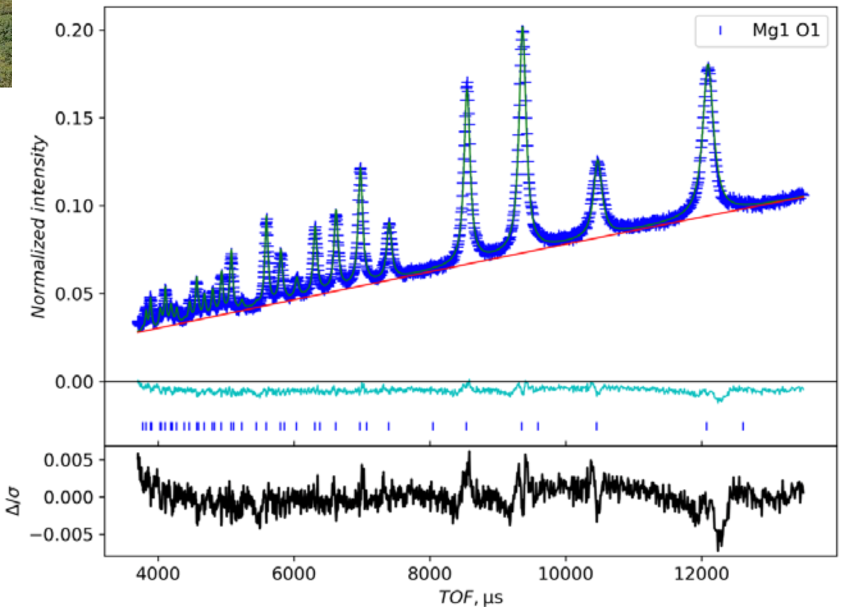
Neutron scattering for catalysis

Peter Metz, Zhenglong Li, Katharine Page ORNL



OAK RIDGE
National Laboratory

Neutrons scattering sensitive to light atoms (i.e., H,D,C,O), as well nanomaterials with well defined local structure

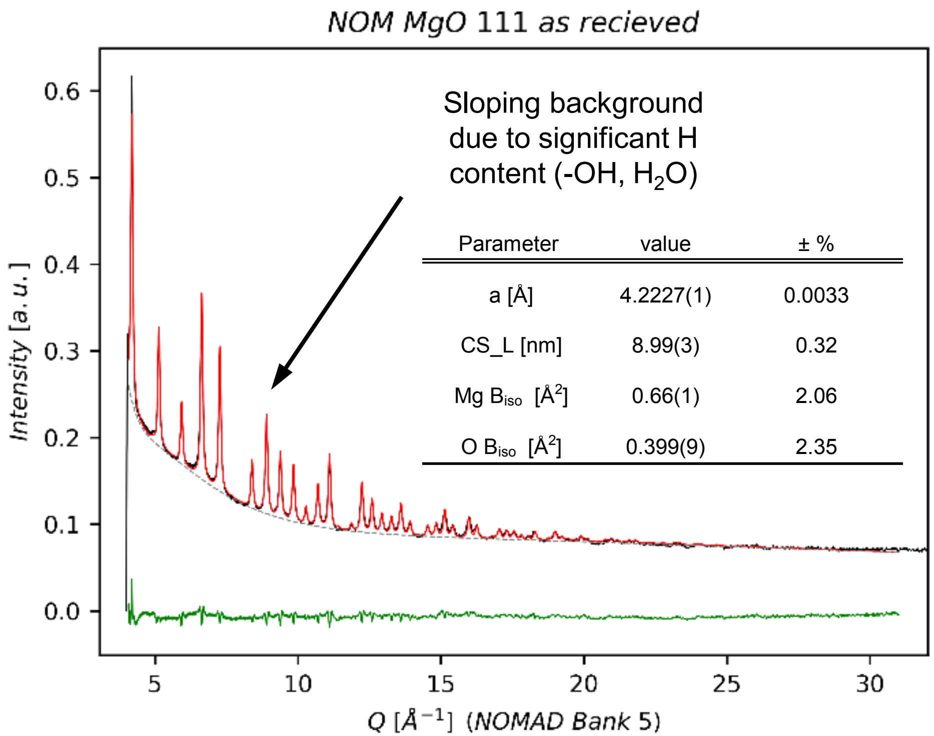


In contrast to DRIFTS and XRD, neutrons have ability to…

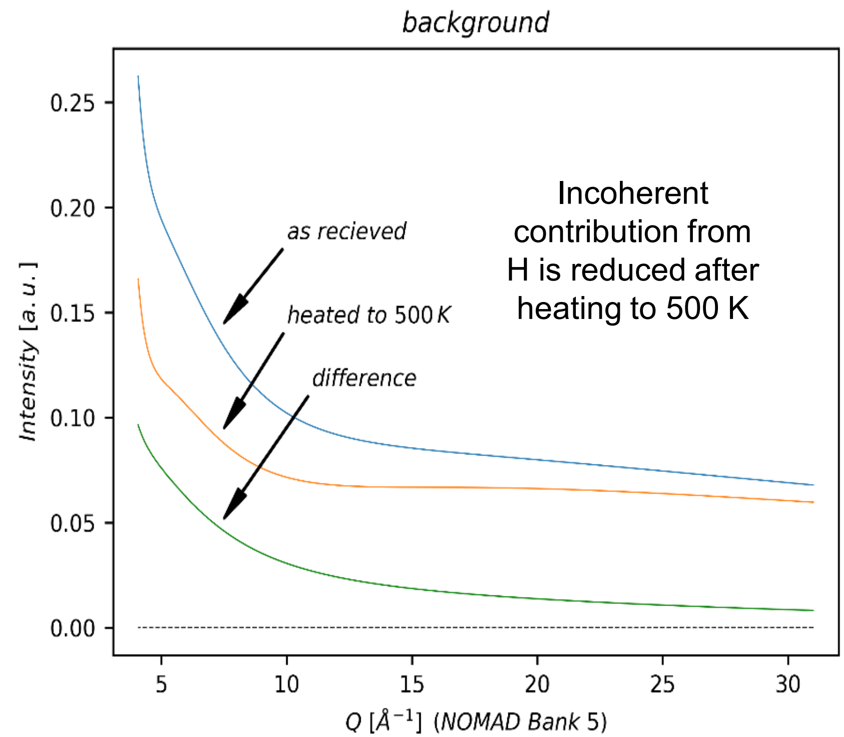
- *distinguish surface -OH, $Mg(OH)_2$, and chemisorbed water in high water vapor*
- *simultaneously characterize surface species and local material structure*

Track H content and local structure

Neutron diffraction & Rietveld analysis: *hydrogen background, lattice parameter (a), crystalline correlation length scale (CS_L), atomic displacement parameters (B_{iso})*



Parameter	value	± %
a [Å]	4.2227(1)	0.0033
CS_L [nm]	8.99(3)	0.32
Mg B_{iso} [Å^2]	0.66(1)	2.06
O B_{iso} [Å^2]	0.399(9)	2.35

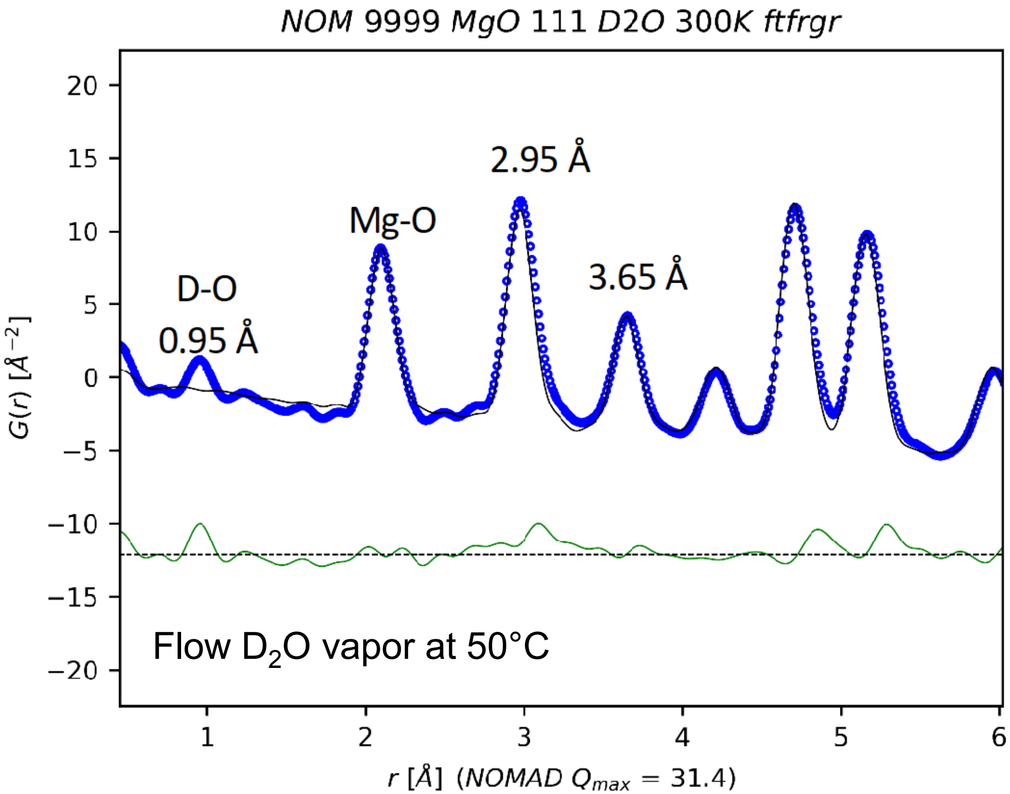


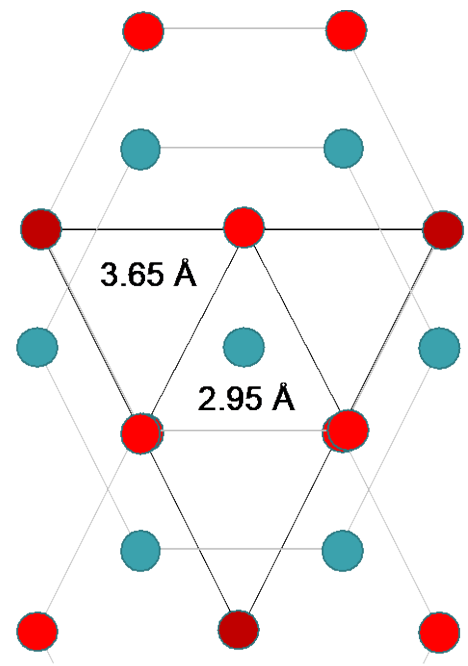
Ability to track degree of surface hydration with *in situ* monitor during steam and heat treatment

Peter Metz, Zhenglong Li, Katharine Page ORNL

Preliminary results D_2O exchange

***Neutron Pair Distribution Function:** interatomic distances (r [Ang]) and number of next-near neighbors (area under curve)*





Oxygen-terminated (111) surface

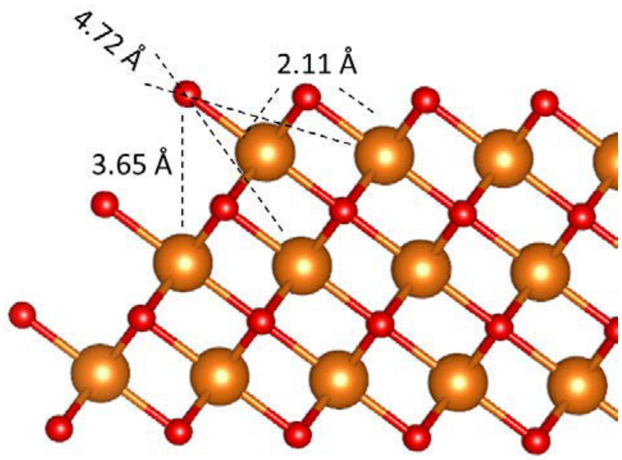
Ongoing work to evaluate surface hydration/dehydration during steam exposure/regen, with particle coarsening

Peter Metz, Zhenglong Li, Katharine Page ORNL

Key Take-Aways and Next Steps

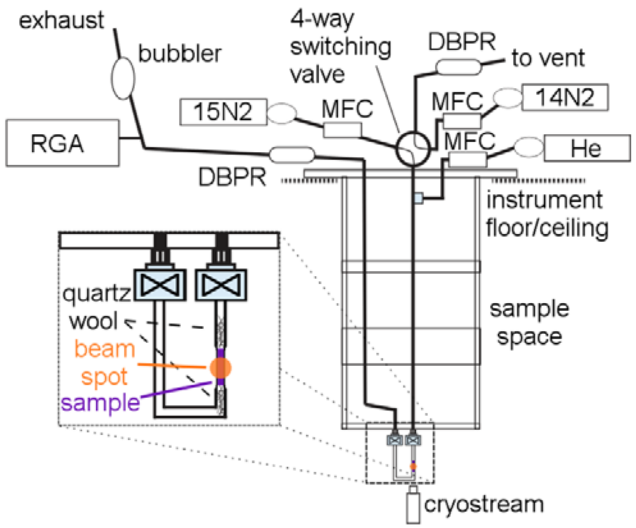
Take-Aways

- MgO(111) displays higher initial activity than MgO(100) for ketone condensation
- Surface hydroxyl groups on MgO(111) facilitate proton transfer and lower key transition states
- Transition to $Mg(OH)_2$ over different facets will be a key consideration for prolonged use



Next Steps

- Need to address the continuous stability and regenerability of MgO(111) morphology and surface termination
- Determine operational process window to maintain target Mg(111)-OH surface



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Let’s discuss!