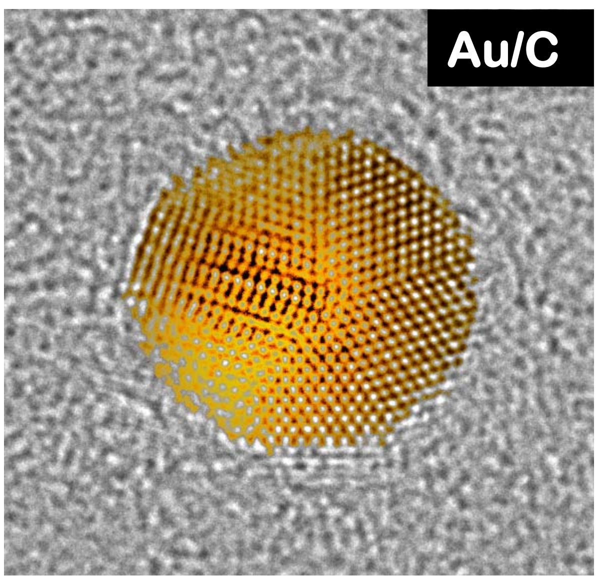
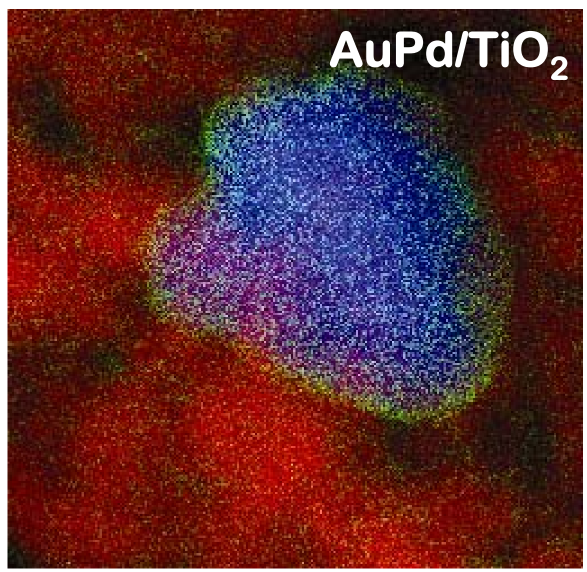
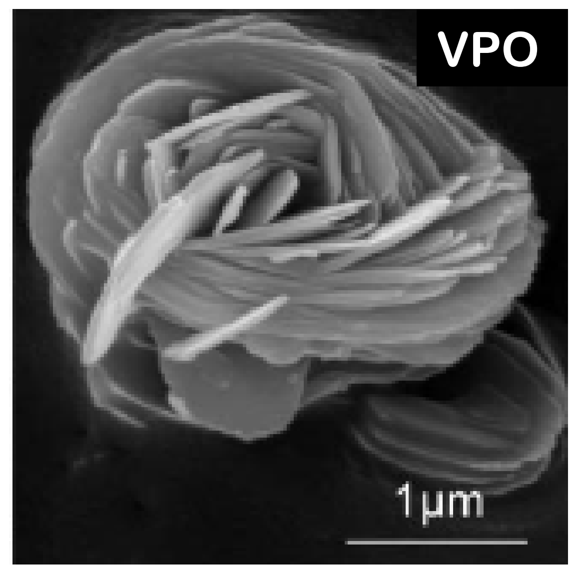
Mixed Oxides in Selective Oxidation Catalysis: The Role of Disordered Surface Layers

Chris Kiely & Andy Burrows
Center for Advanced Materials and Nanotechnology, Lehigh University







Acknowledgements

Graham Hutchings, Leverhulme Catalysis Centre, Cardiff University, UK

Jose Calvino, Departmento de Quimica Inorganica, Cadiz University, Spain

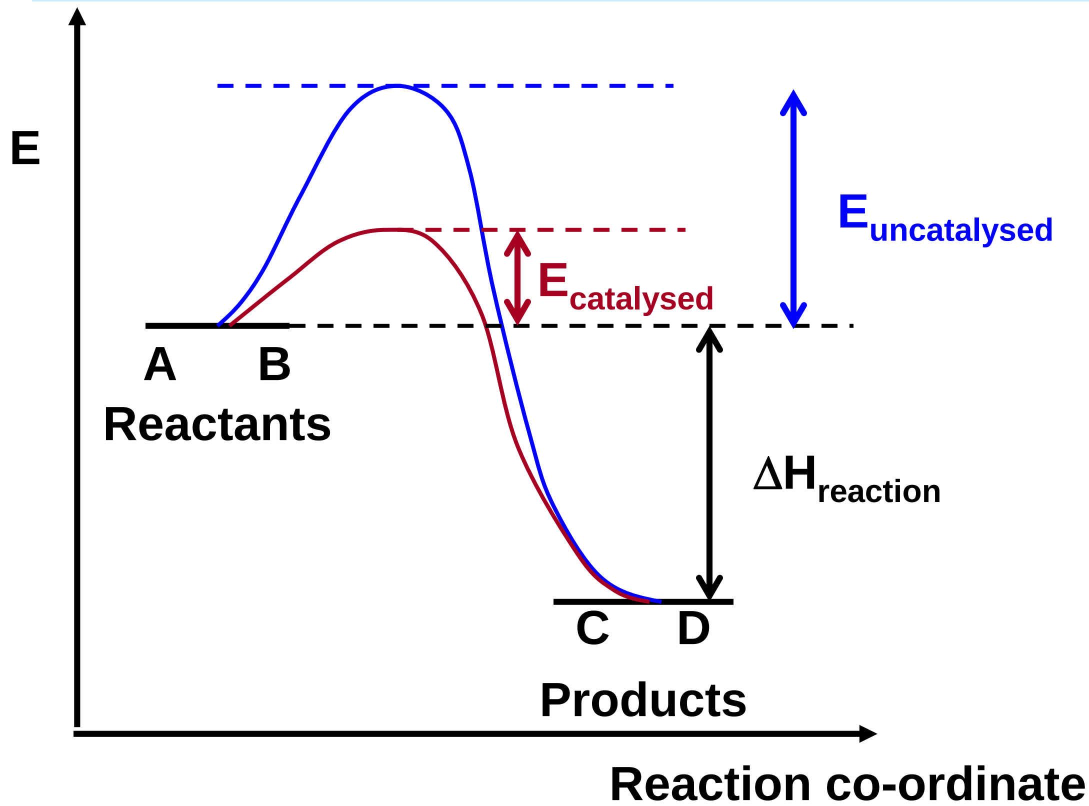
Jean Claude Volta, Claude Mirodatos, Institut de Recherches sur la Catalyse, Lyon, France

Jens Perregaard, Poul Hojlund Neilson, Haldor Topsoe, Copenhagen, Denmark

Robert Schlogl, Fritz Haber Institute, Berlin, Germany

Catalysis 101

A catalyst is a substance that increases the rate at which a chemical system reaches equilibrium without being consumed in the process.



Conversion - the fraction of reactants that are converted to products.

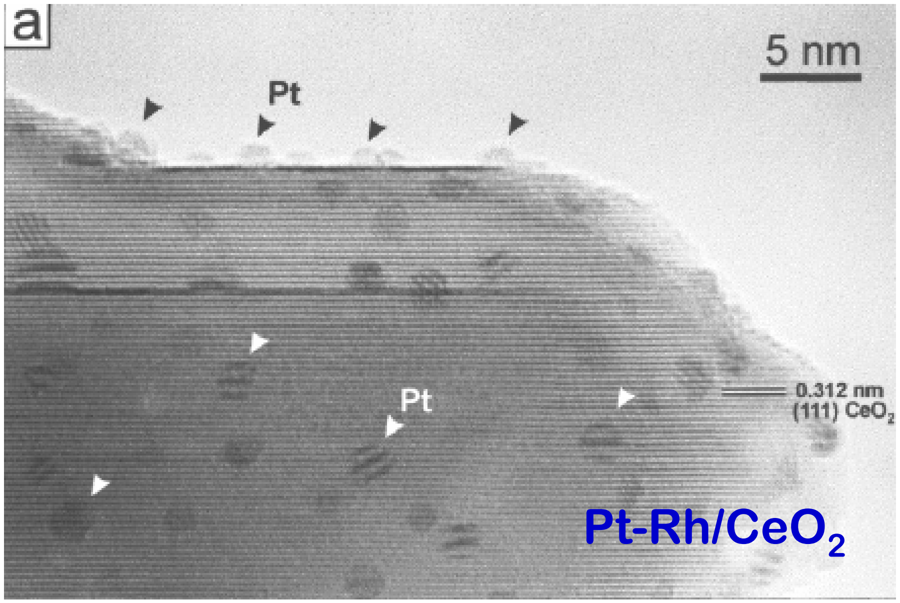
Selectivity - the fraction of desired product produced.

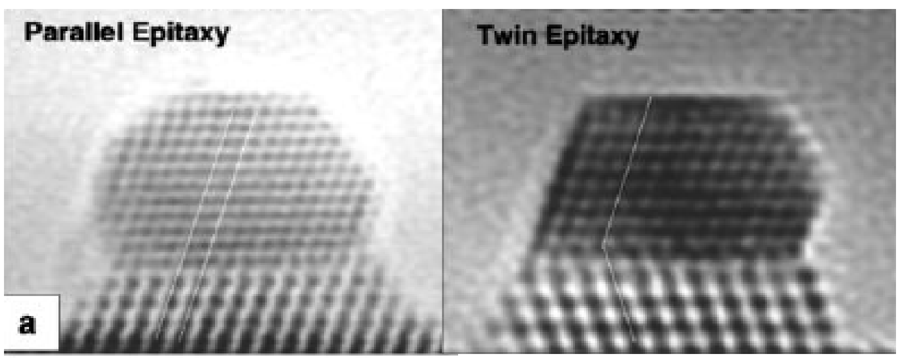
Lifetime - the time period before a catalyst has to be replaced.

The catalyst tends to provide an alternate reaction pathway with a lower activation energy.

Types of Heterogeneous Catalysts

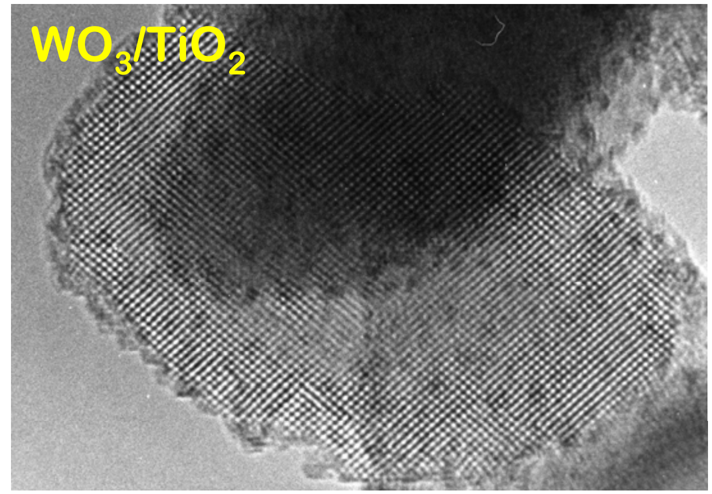
Supported Metals

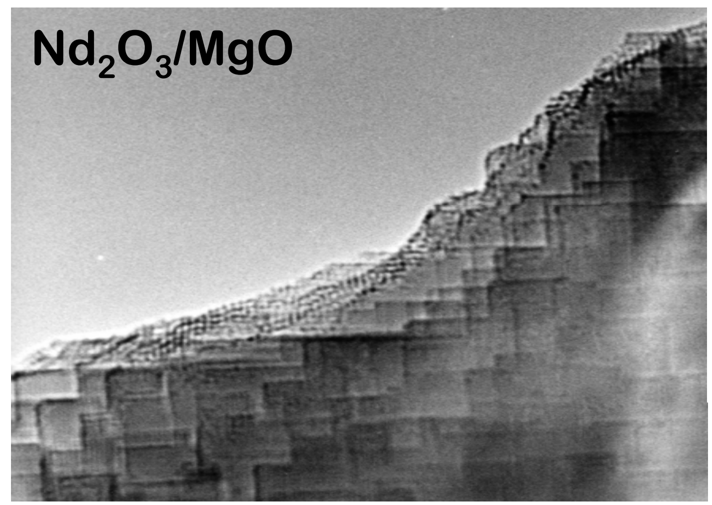




e.g. Automotive CO oxidation catalysts

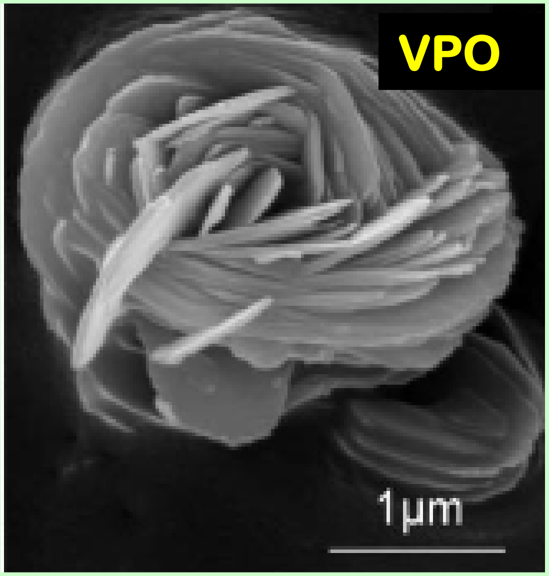
Supported Oxides

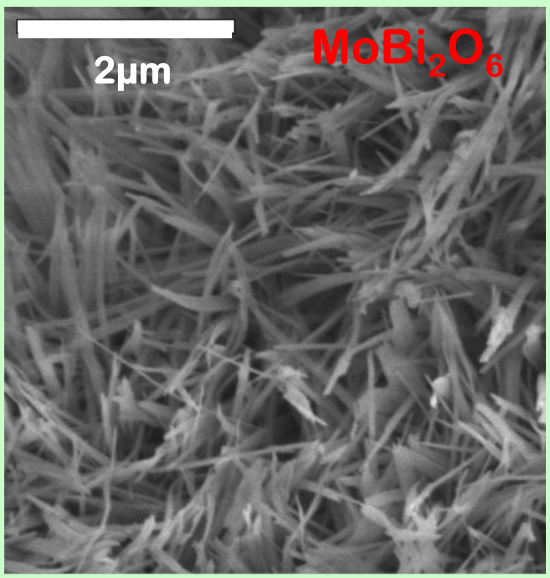




e.g. Selective Catalytic Reduction of NO_x

Mixed Oxide Catalysts – Selective Oxidation

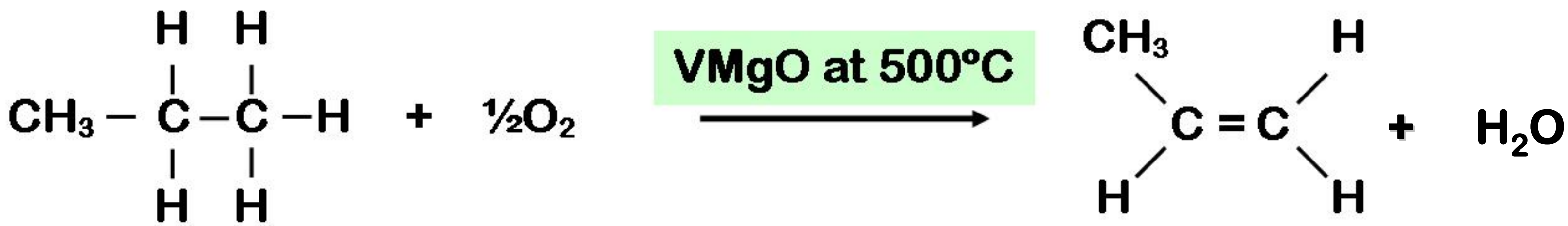




Reactant		Product	Catalyst
n-butane	→	maleic anhydride	VPO
propane	→	propene	VMgO
propene	→	acrolein	$FeSbO_4$
propene	→	acrylonitrile	$MoBi_2O_6$
butene	→	butadiene	$MoBi_2O_6$

Oxidative Dehydrogenation of Propane (ODHP)

Desirable



Undesirable

$$C_3H_8 \quad + \quad 5O_2 \longrightarrow 3CO_2 \; + \; 4H_2O$$

- 14wt% V in catalyst gives optimum performance
- Propane (C_3H_8) conversion efficiency –11%
- Propene (C_3H_6) selectivity – 80%

Propene (C_3H_6) is an important feedstock chemical for the manufacture of isopropanol, acrolein, acrylic acid and acrylonitrile.

Catalyst Preparation Procedure

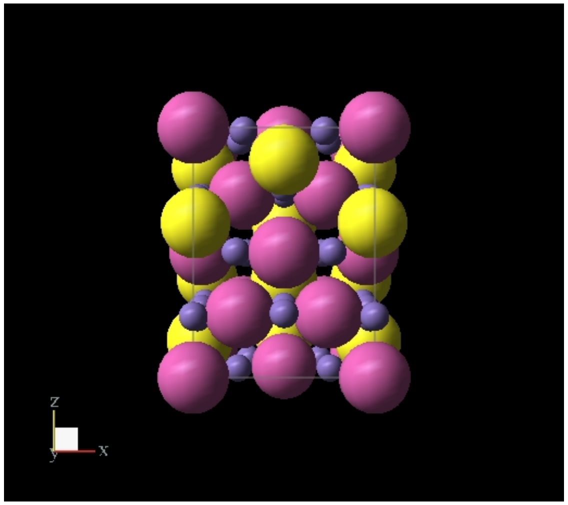
- $Mg(OH)_2$ precipitated from magnesium nitrate solution using KOH
- Precipitate filtered off, purified and crushed
- $Mg(OH)_2$ added to hot ammonium metavanadate (NH_4VO_3)
- Suspension evaporated to dryness leaving VMgO catalyst
- Calcined in O_2 at 550°C (6h) and then at 800°C (6h)

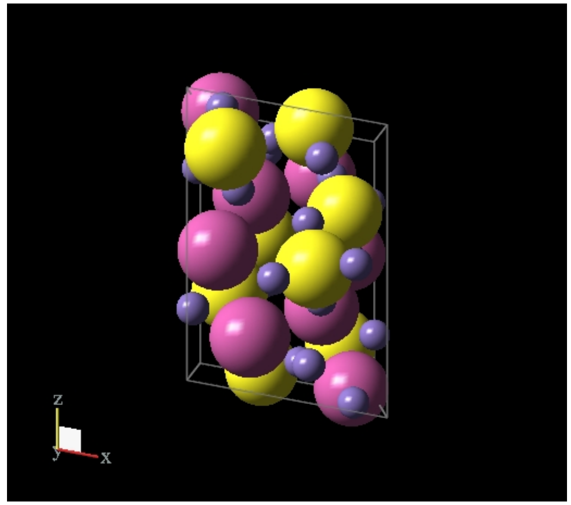
Reaction Conditions

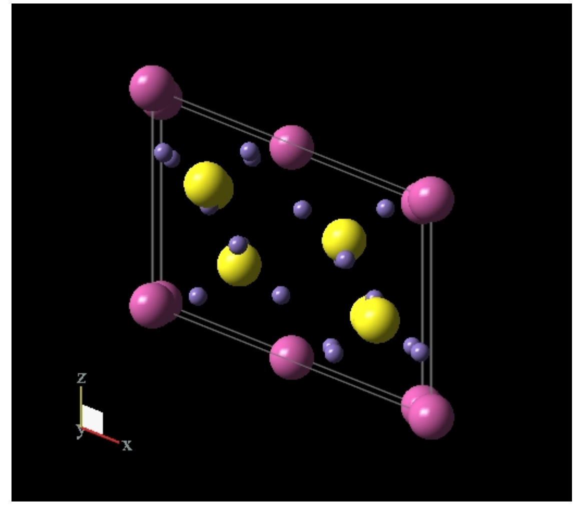
Fixed bed reactor: 500-550°C : atmospheric pressure

C_3H_8 / O_2 / He : 1.0 / 0.1 / 98.9

Mixed VMgO (V^{5+}) Phases







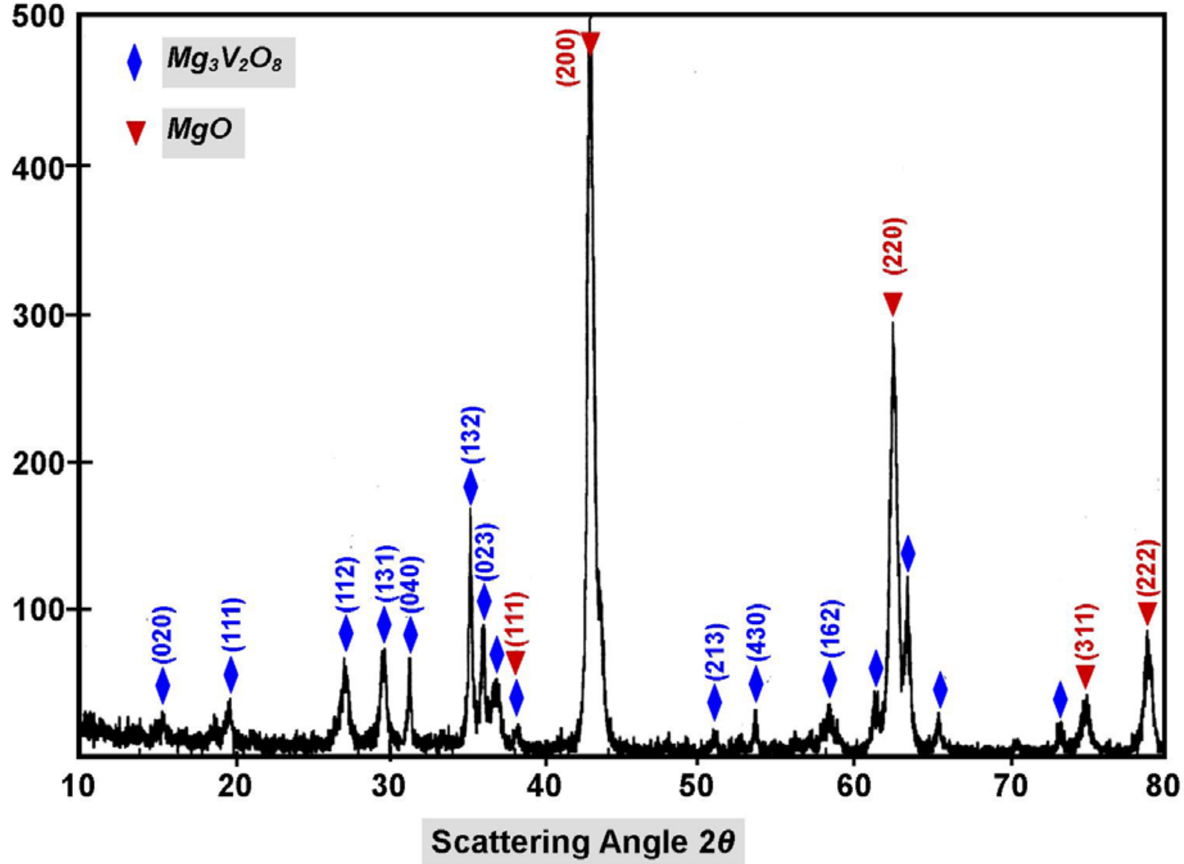
$Mg_3V_2O_8$
Ortho-vanadate
Cmca (64)
Orthorhombic (mmm)

$Mg_2V_2O_7$
Pyro-vanadate
P21/c (14)
Monoclinic (2/m)

MgV_2O_6
Meta-vanadate
C2/m (12)
Monoclinic (2/m)

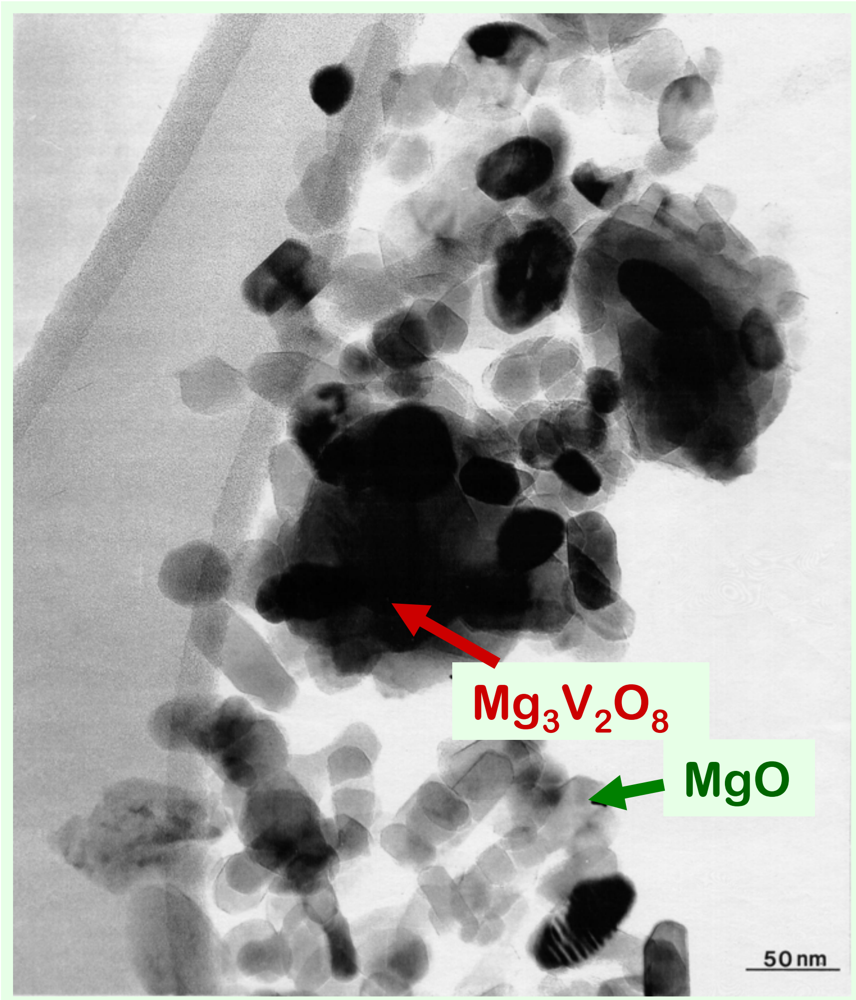
In isolation, *none* of the pure VMgO phases is particularly active or selective for the oxidative dehydrogenation of propane.

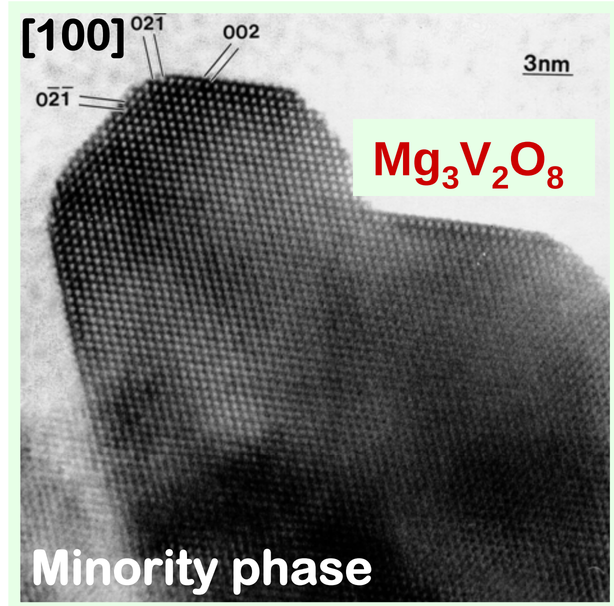
XRD of the 14V/VMgO Catalyst

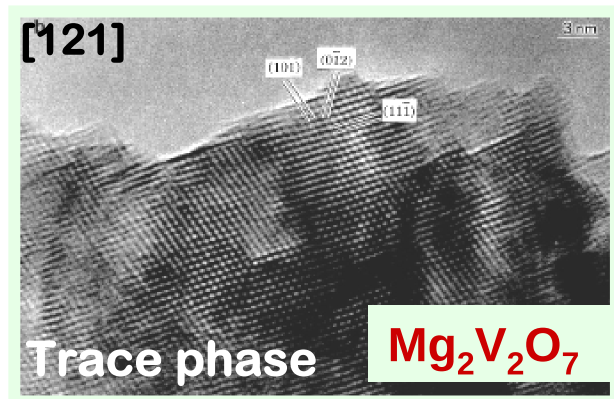


- To study the interactions between the constituent phases of the VMgO catalyst
- To follow any structural changes that occur under typical reaction conditions

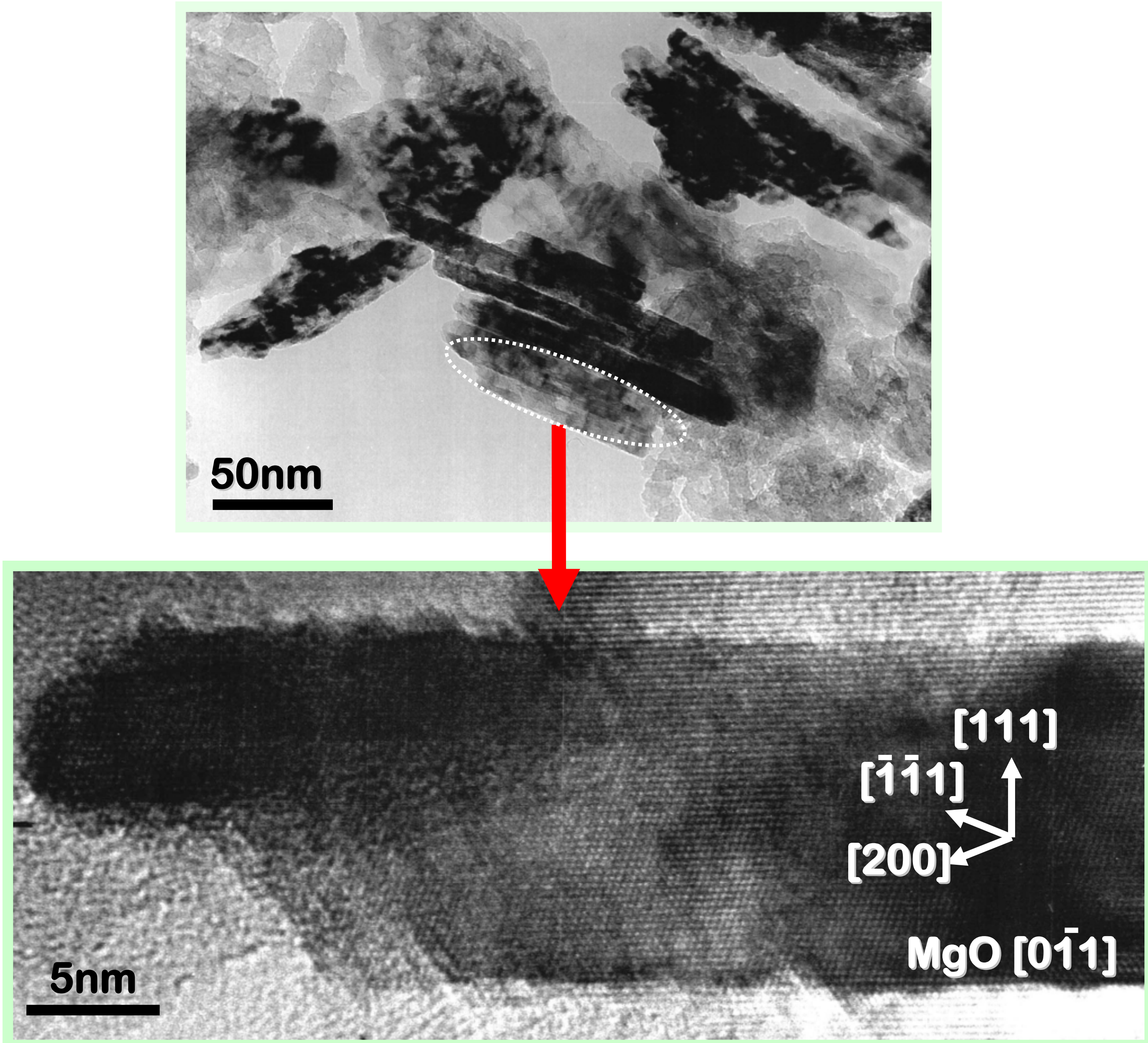
Microstructure of the 14V/VMgO Catalyst



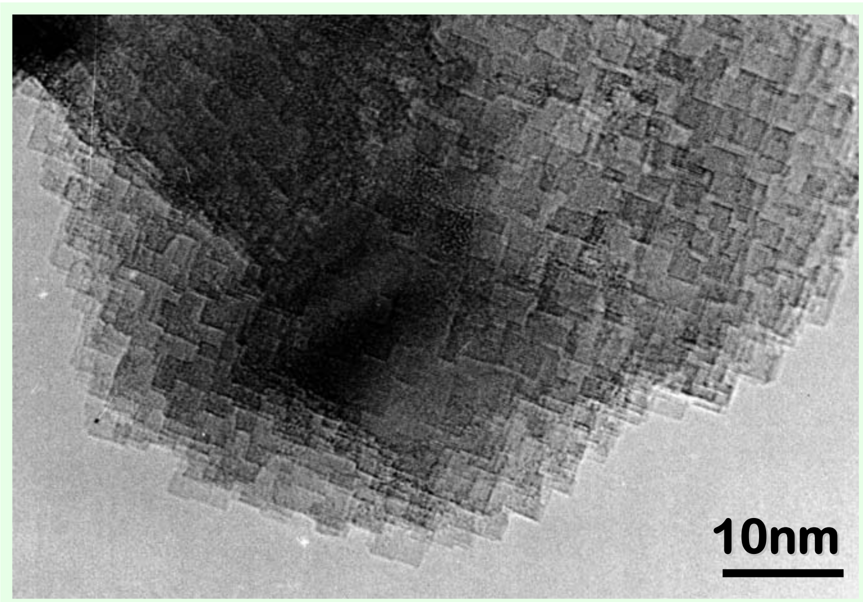


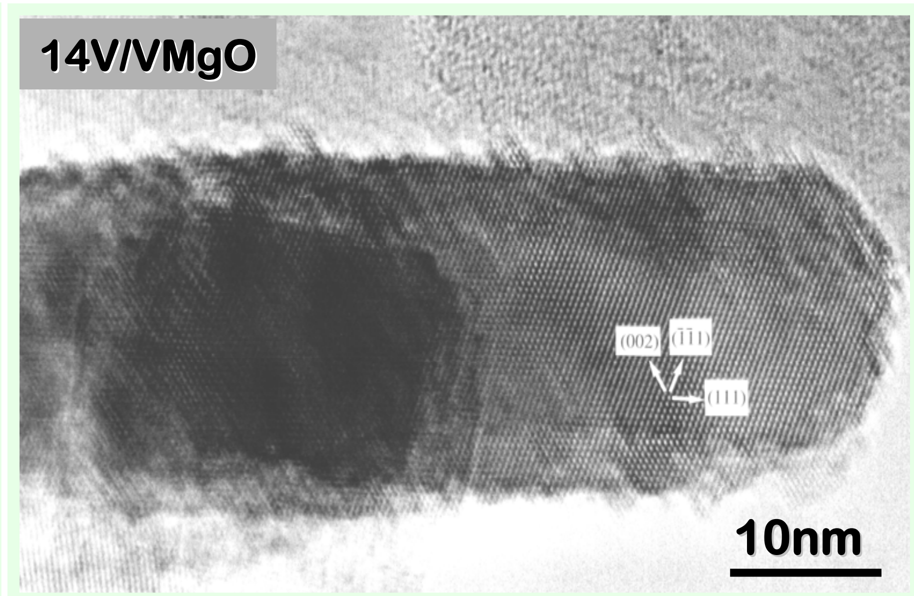


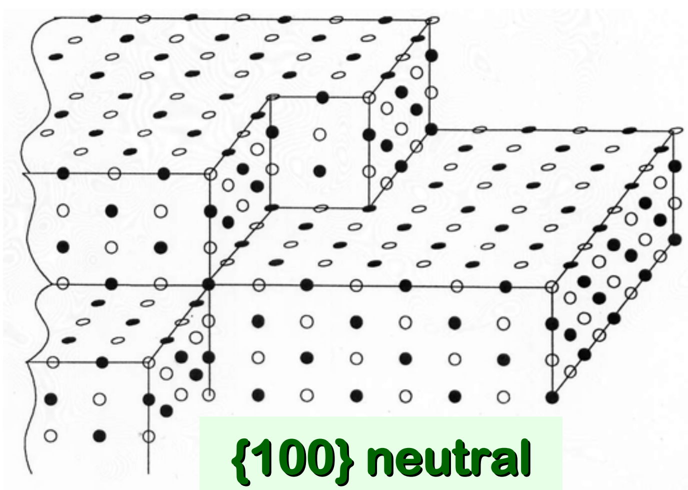
MgO Component of the 14V/VMgO Catalyst



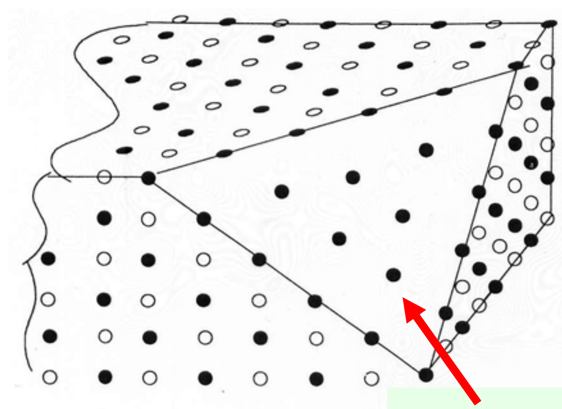
MgO Facet Structure





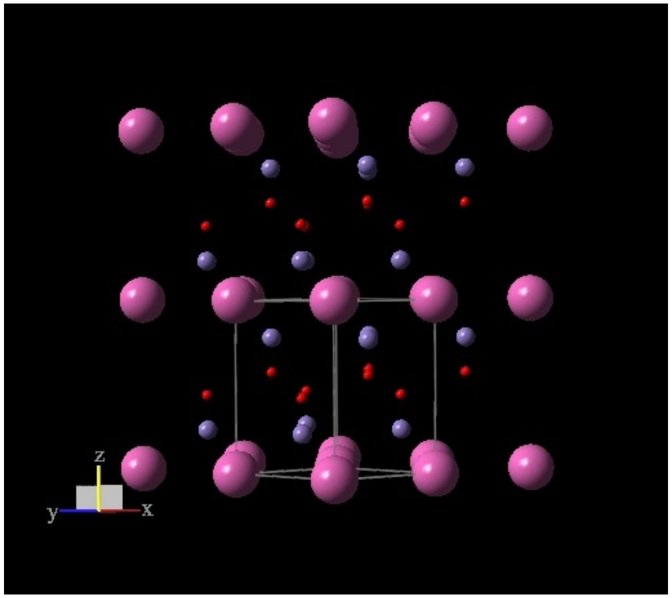


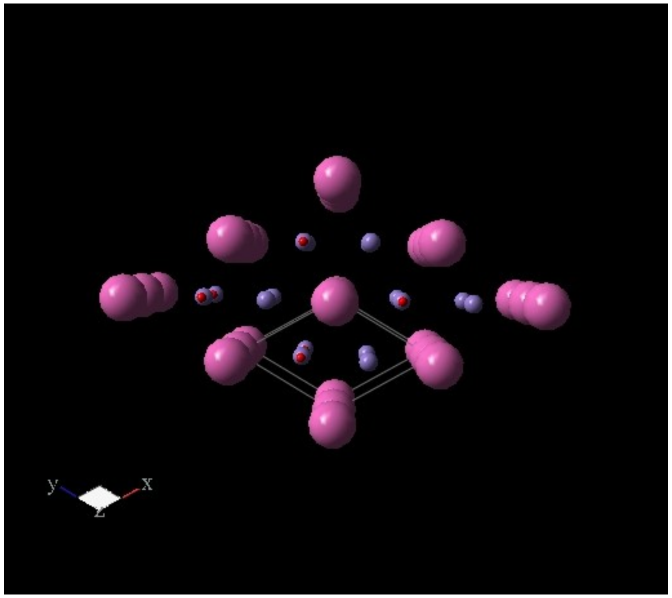
{100} neutral facets



{111} polar facet

Brucite – $Mg(OH)_2$ | Magnesia - MgO

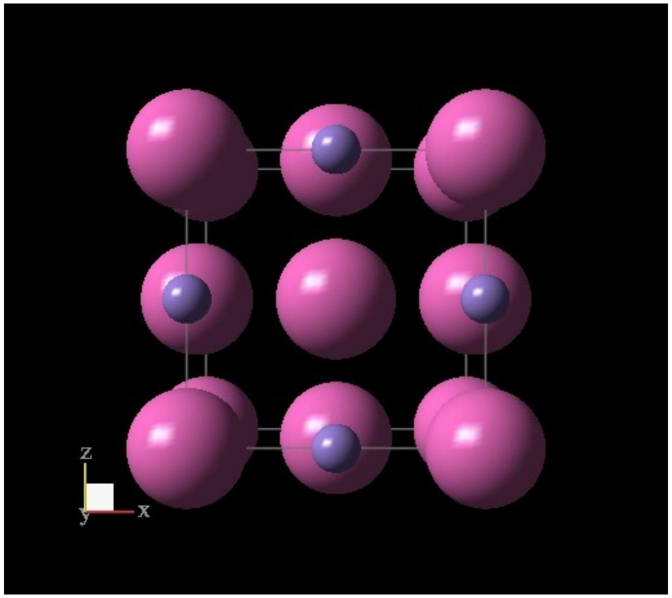


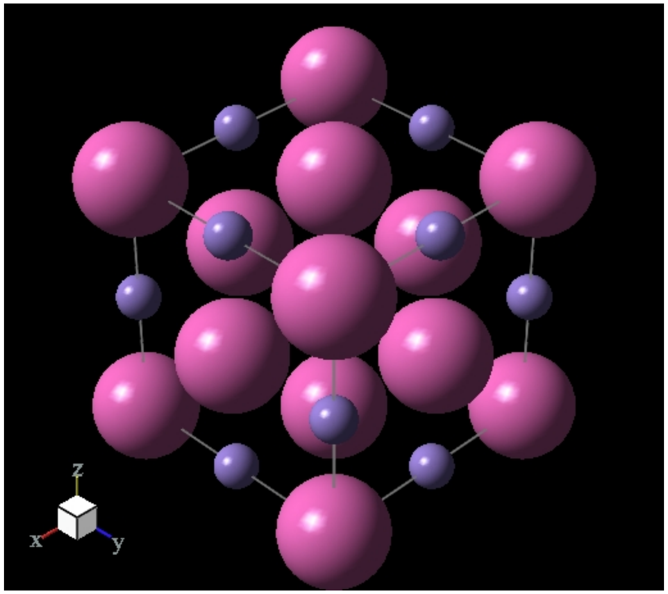


Hexagonal

a=0.314nm

c=0.476nm

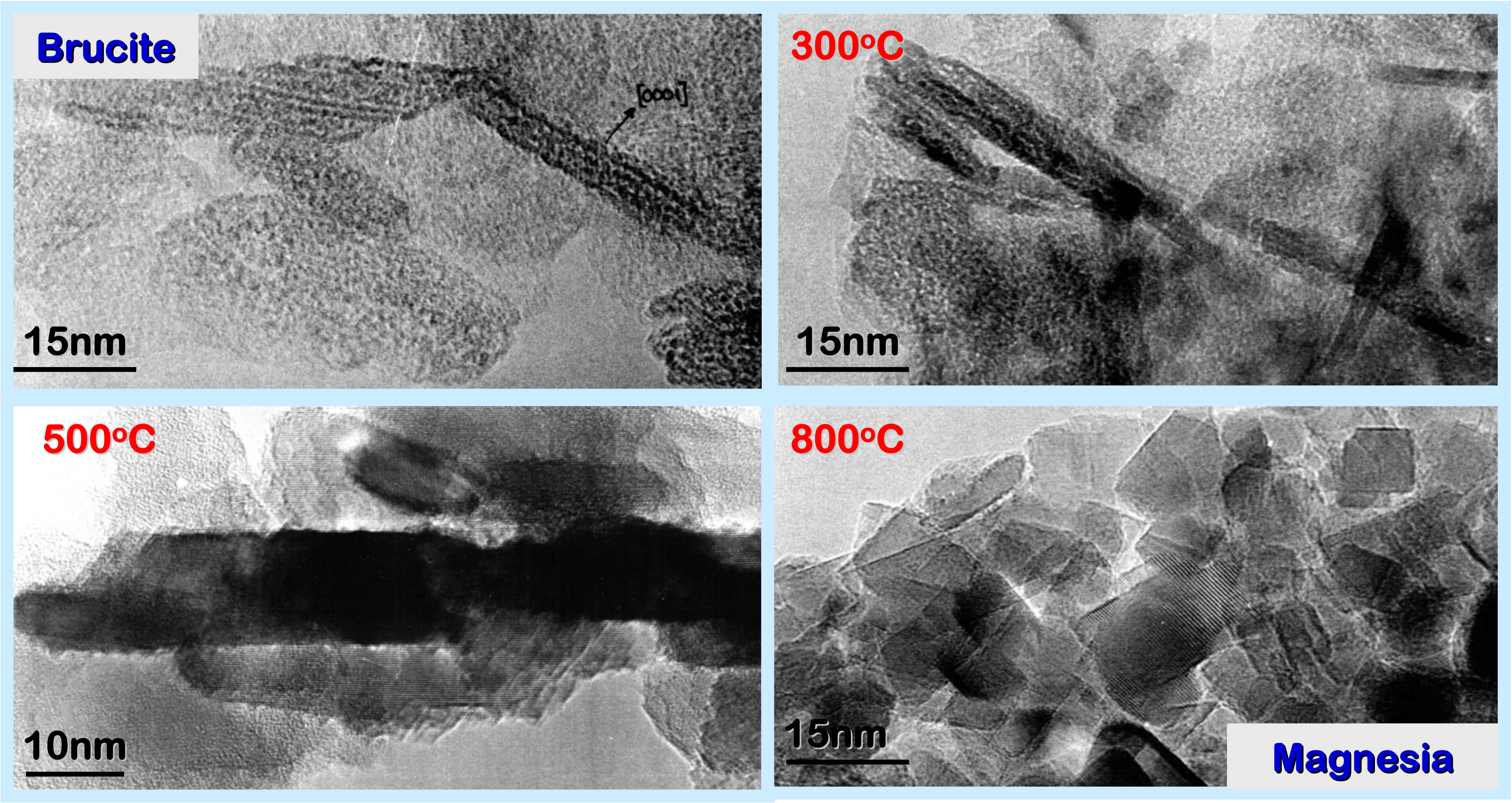




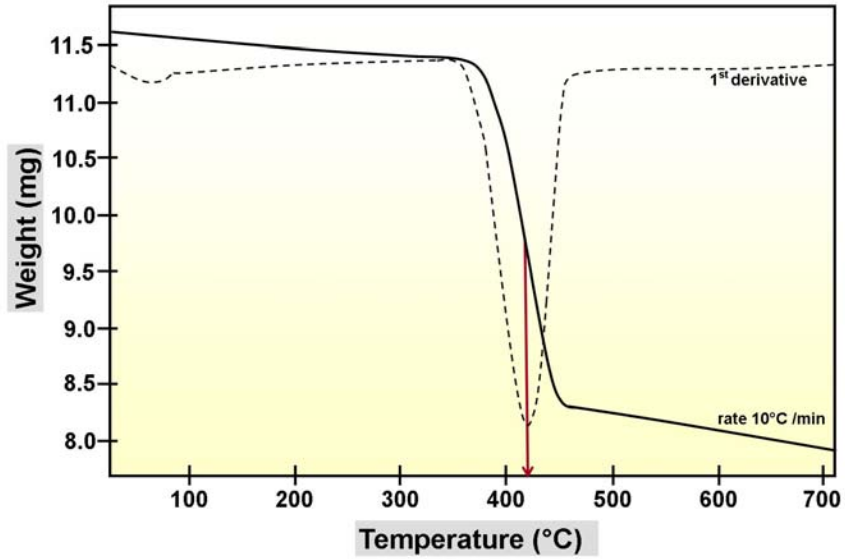
Cubic

a=0.423nm

Brucite to Magnesia Transformation

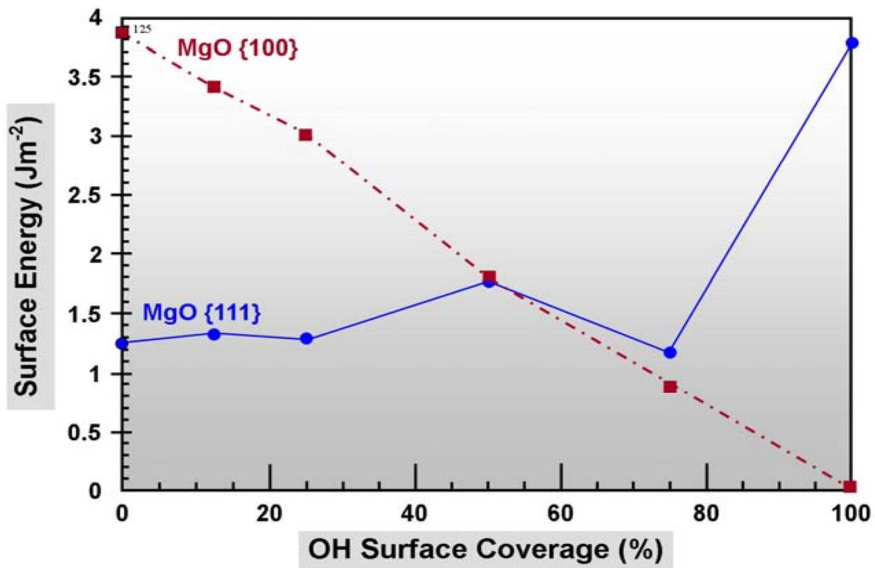


Thermogravimetric analysis of brucite decomposition



30wt% weight loss at ~420^{o}C as water of hydration is lost

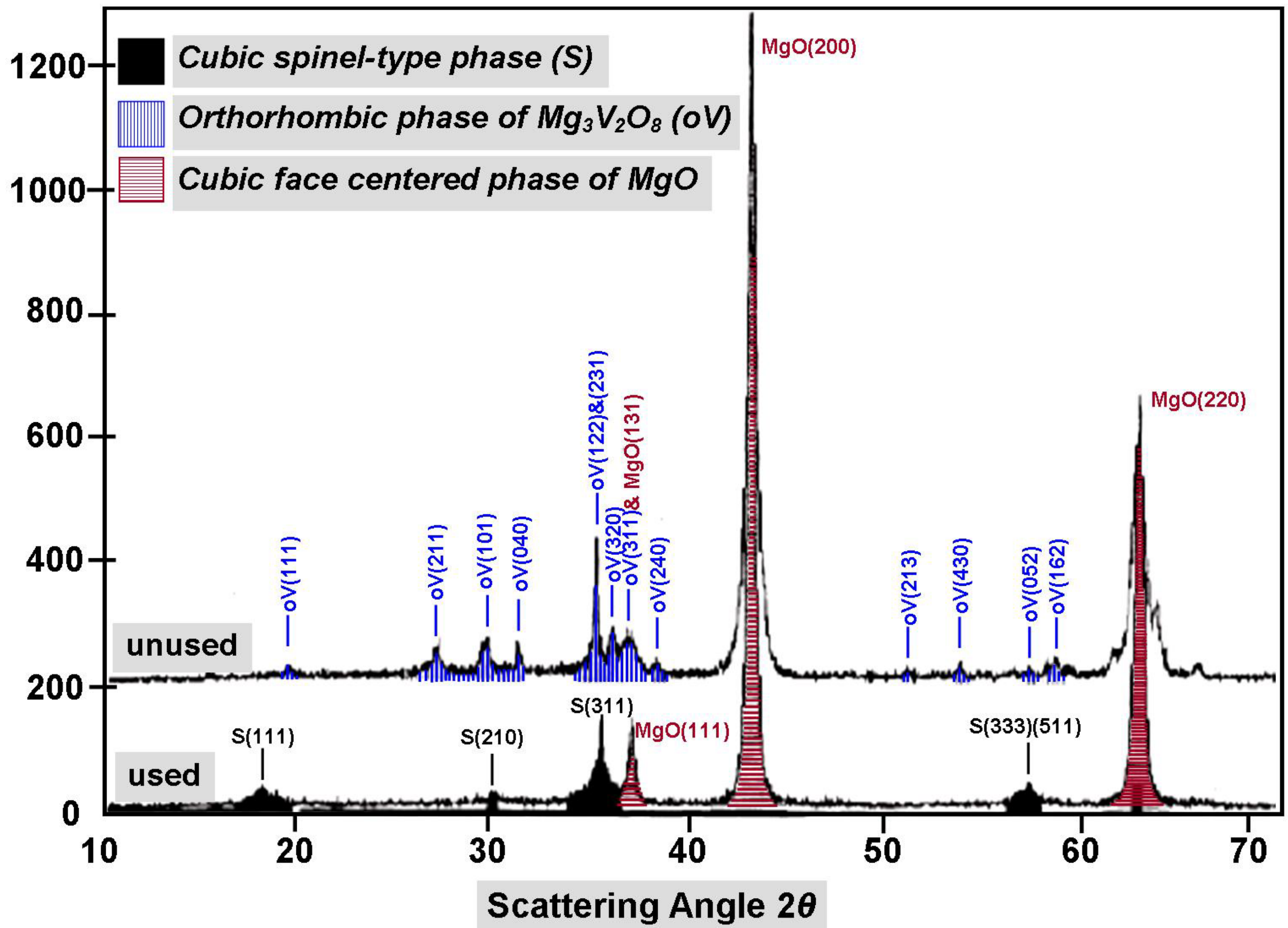
Relative stability of hydroxylated MgO surfaces



Polar surface stabilized a adsorbed –OH groups

De Leeuw et al. *J.Phys.Chem,* 99, (1995), 17219

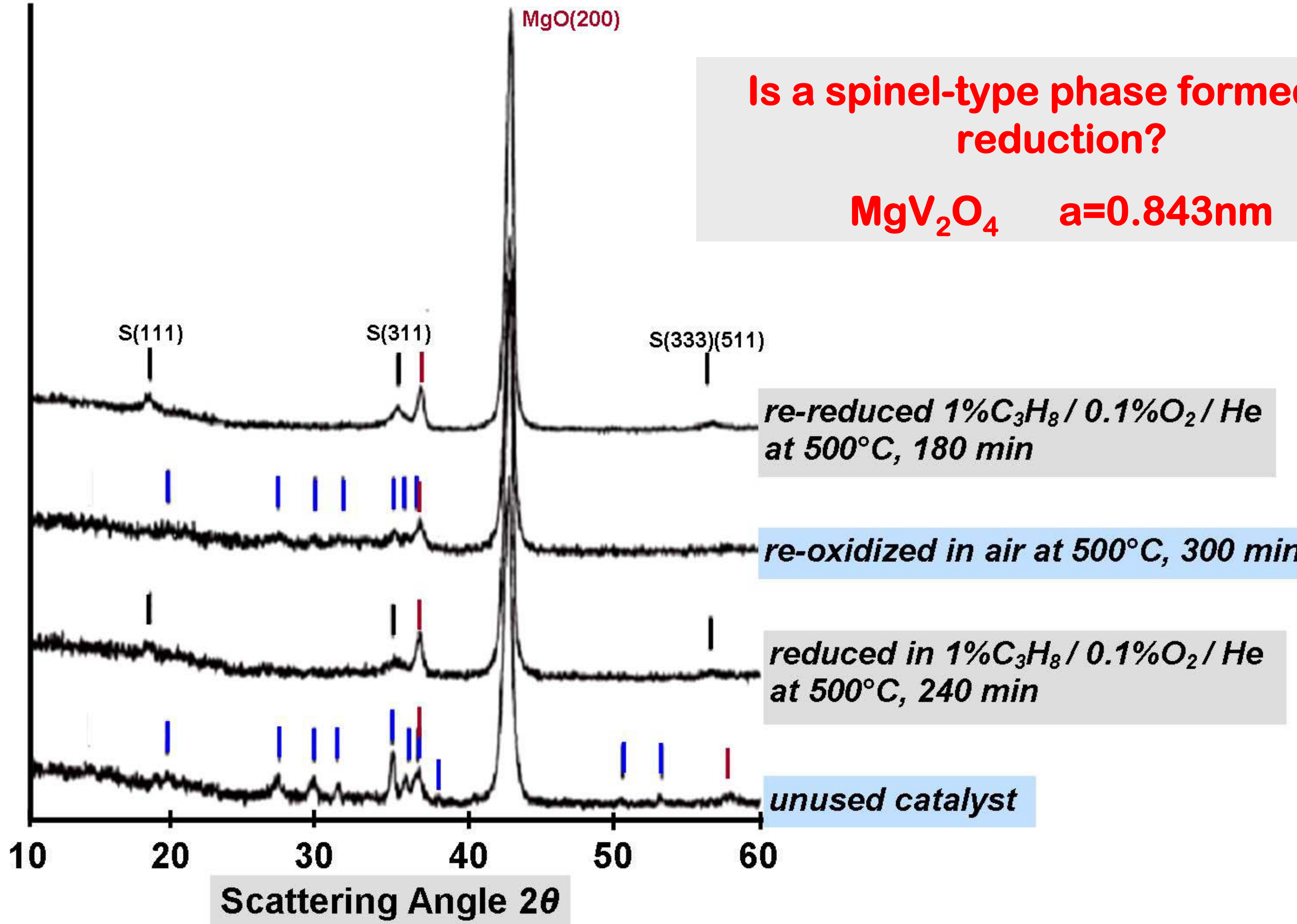
XRD comparison of the 14V/VMgO catalyst in the unused and used state



In-situ XRD analysis of the 14V/VMgO catalyst under redox cycling

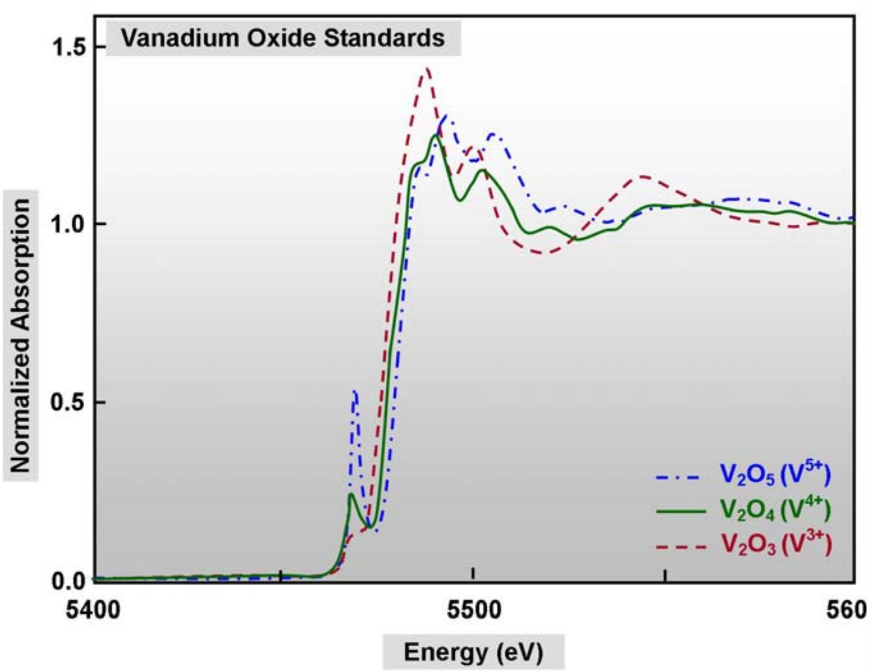
Is a spinel-type phase formed on reduction?

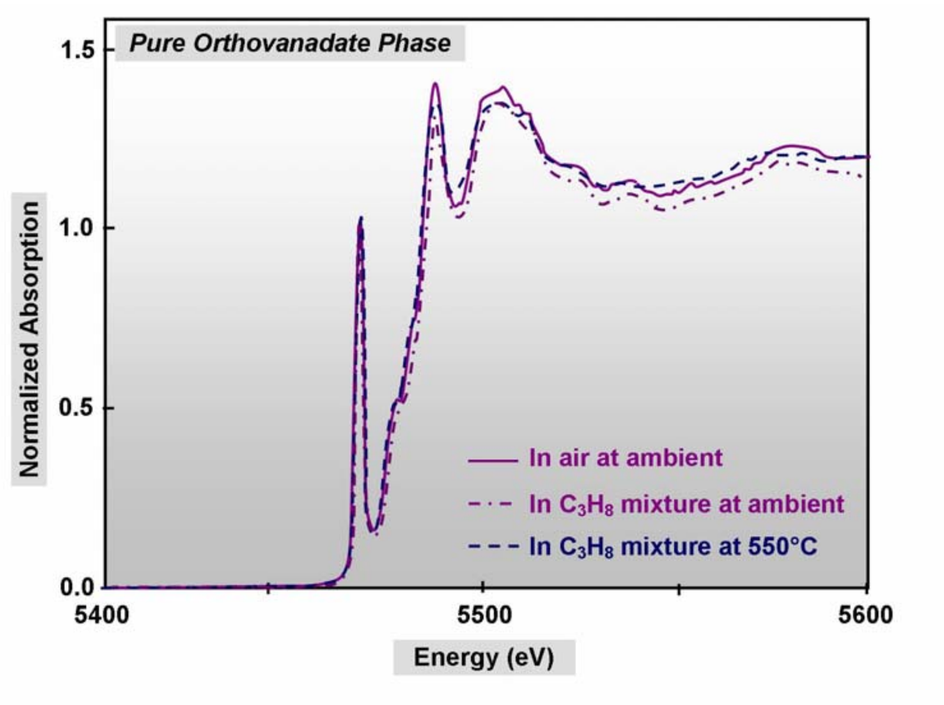
MgV_2O_4 a=0.843nm



EXAFS of standard phases

XANES of the V K-edge





V_2O_3 (V^{3+})

V_2O_4 (V^{4+})

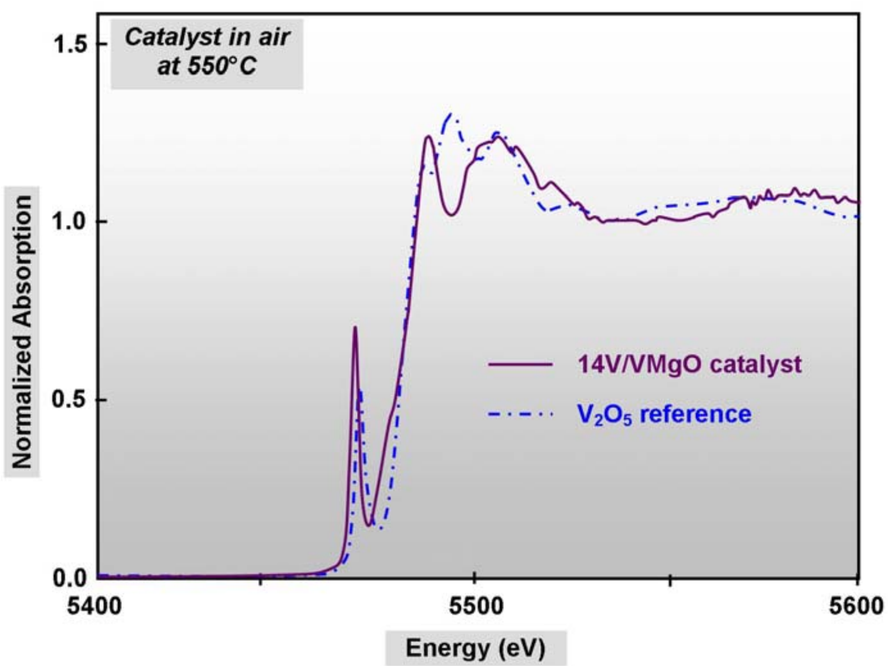
V_2O_5 (V^{5+})

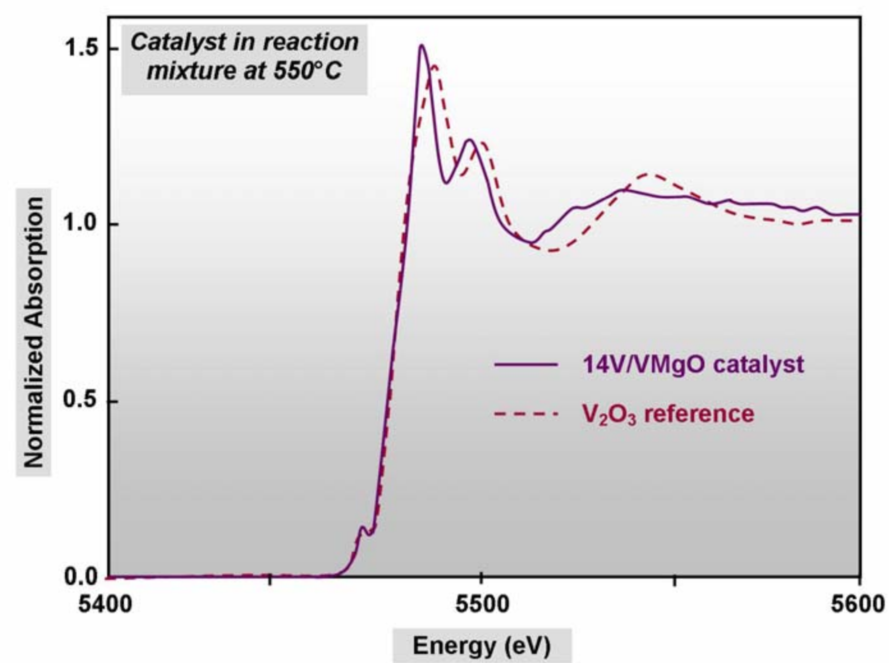
Pure $Mg_3V_2O_8$

Looks like V^{5+} in the unused and used state

In-situ EXAFS of the 14V/VMgO catalyst

XANES of the V K-edge





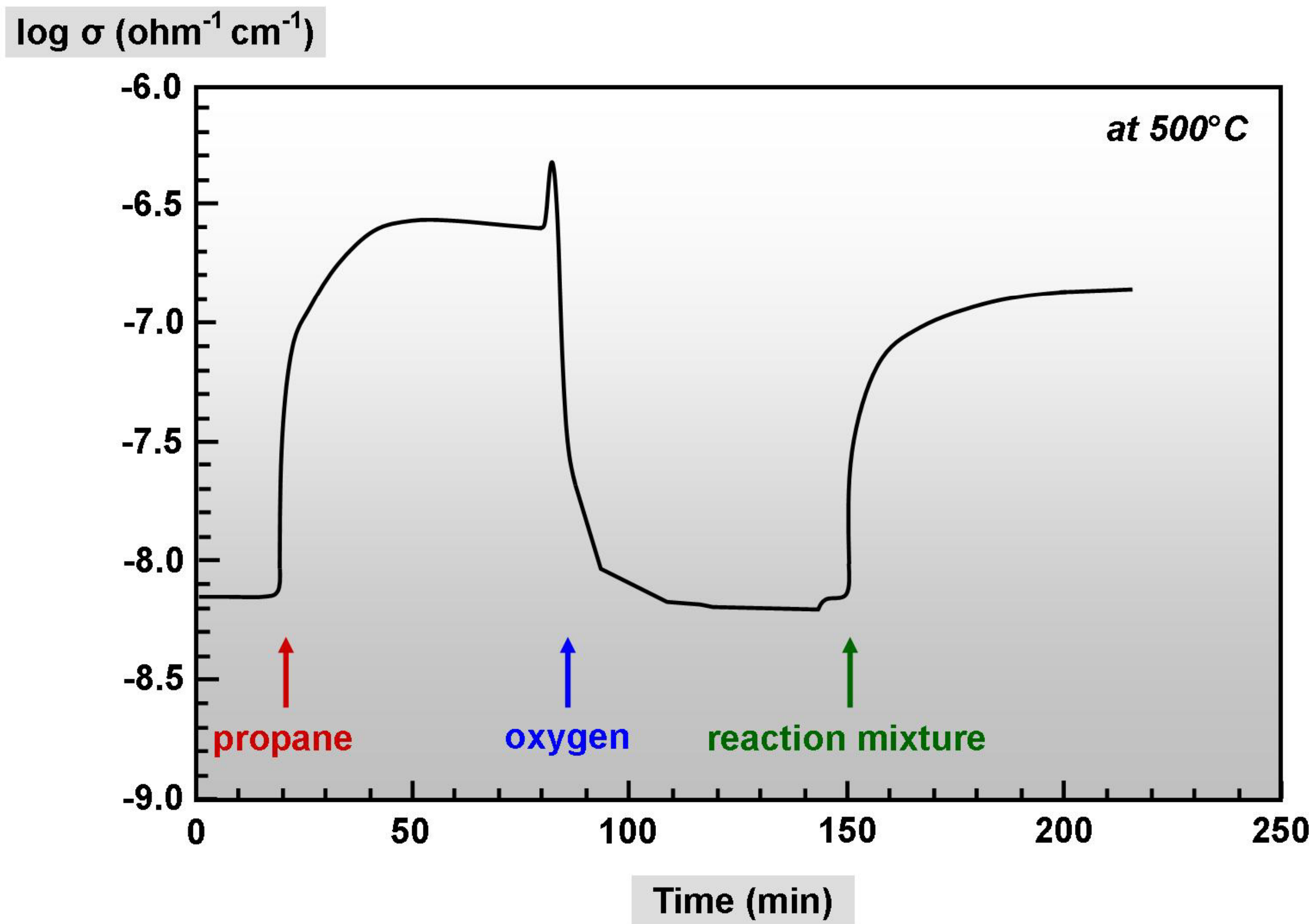
14V/VMgO in air @ 500^{o}C

Resembles V^{5+} in the unused state

14V/VMgO in reaction mixture @ 500^{o}C

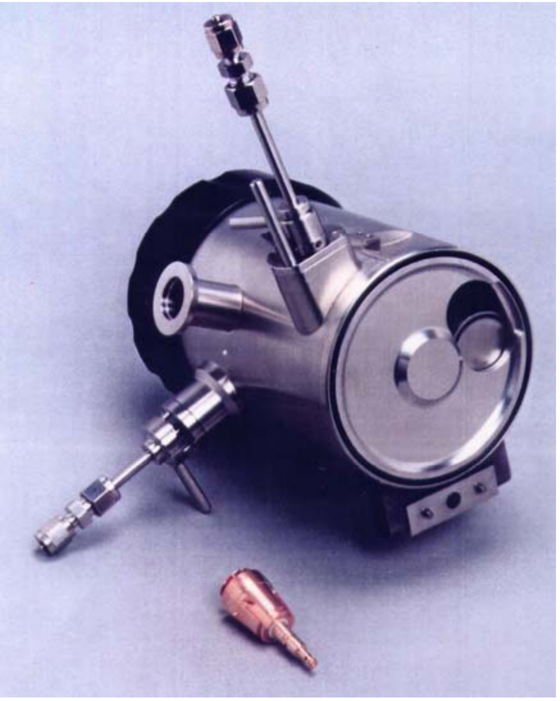
Resembles V^{3+} in the used state

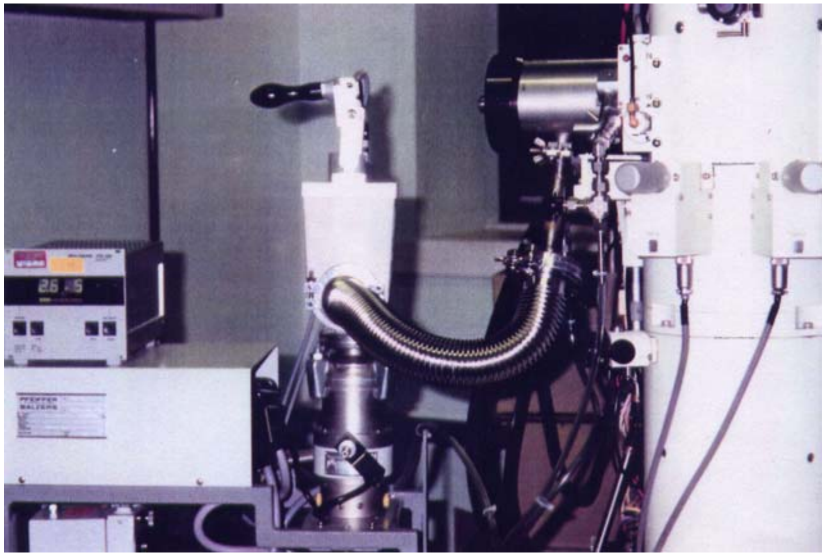
In-situ electrical conductivity measurements on the 14V/VMgO catalyst

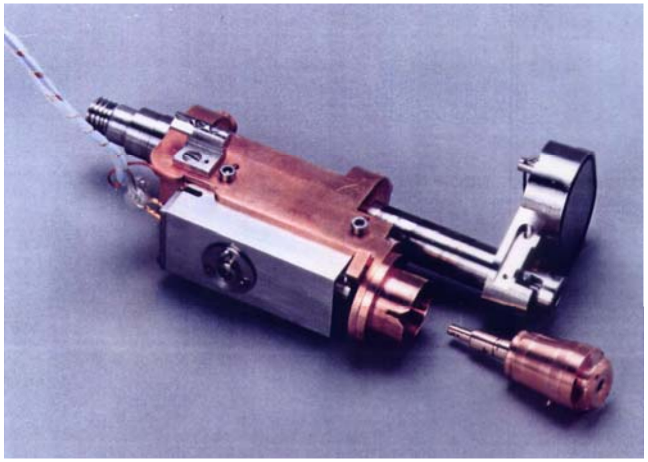


Increased n-type conductivity observed on reduction

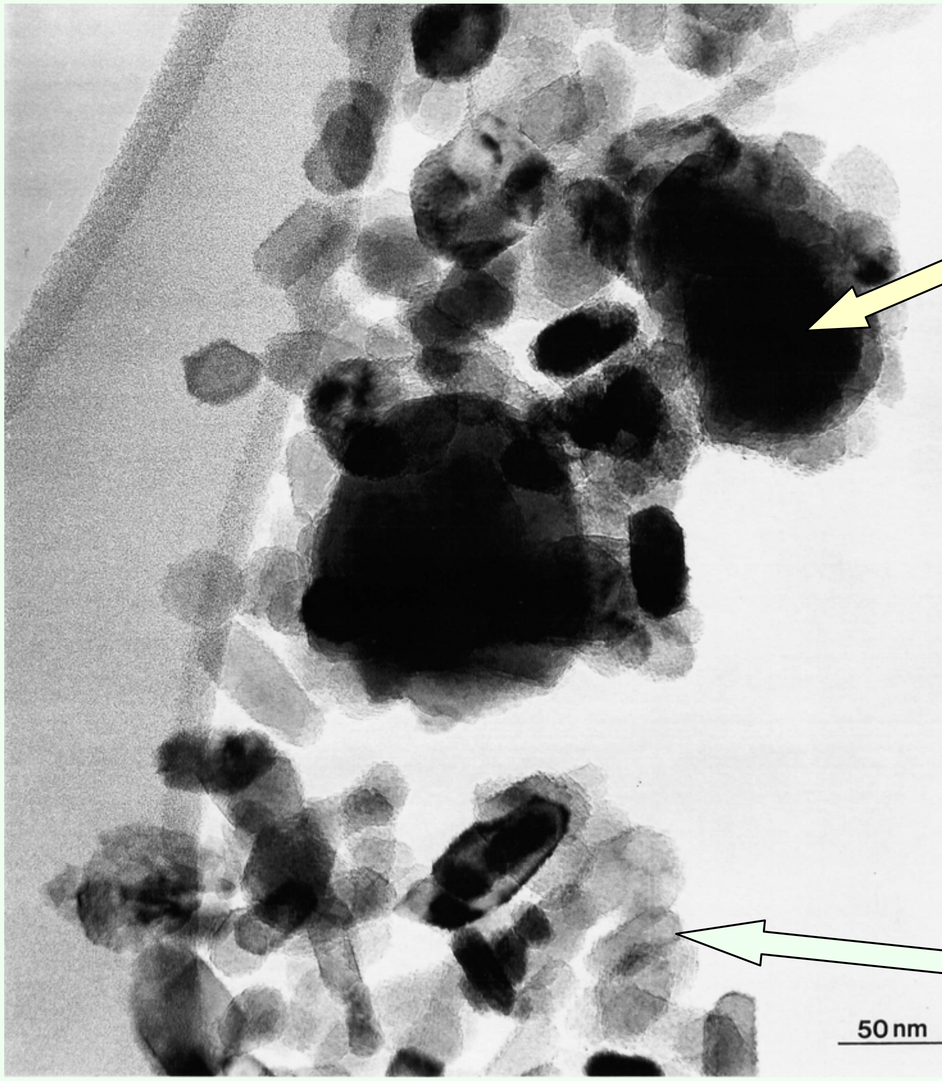
Ex-situ gas reaction cell for JEOL 2000EX HREM







Reminder : 14V/VMgO catalyst microstructure



~10 vol% of catalyst consists of $Mg_3V_2O_8$

XEDS analysis

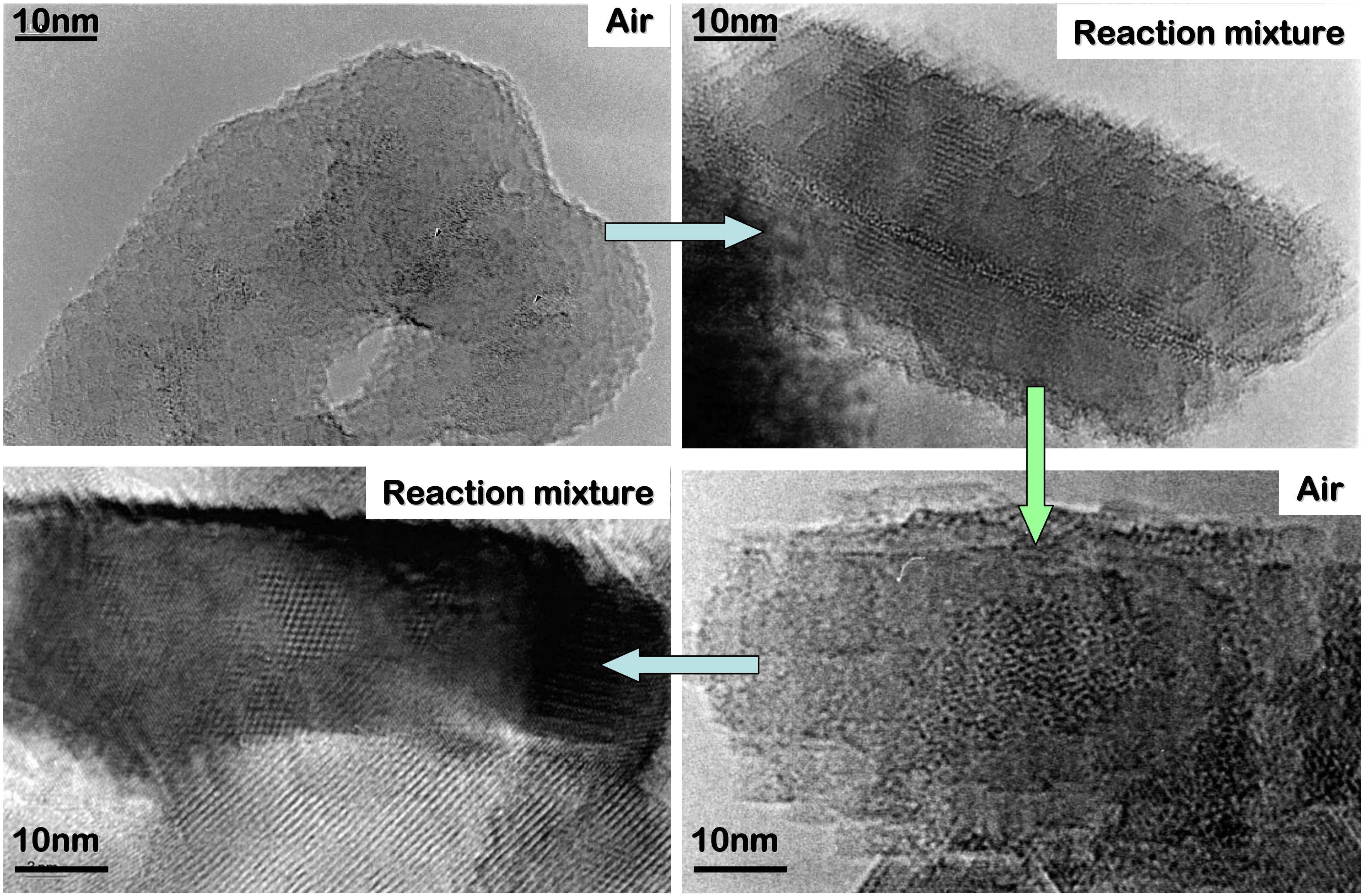
Mg : V
3 : 2

~90 vol% of catalyst consists of MgO

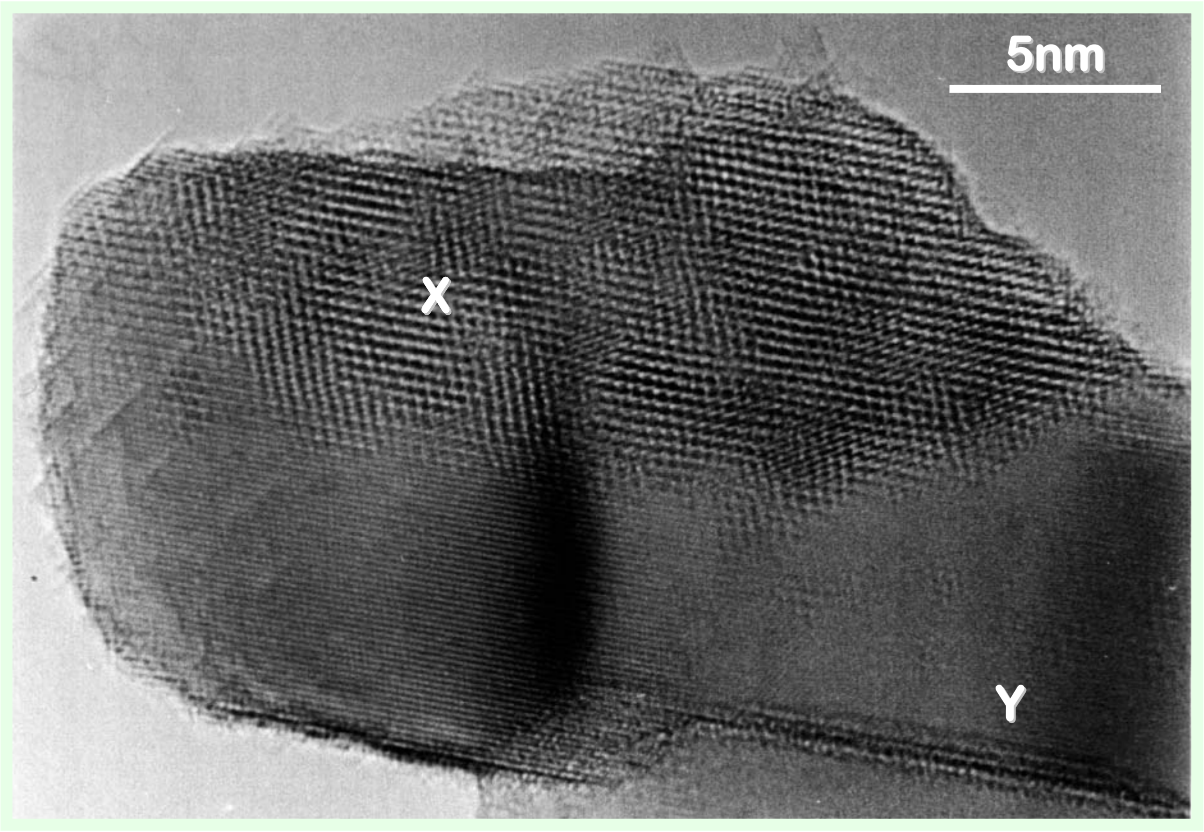
XEDS analysis

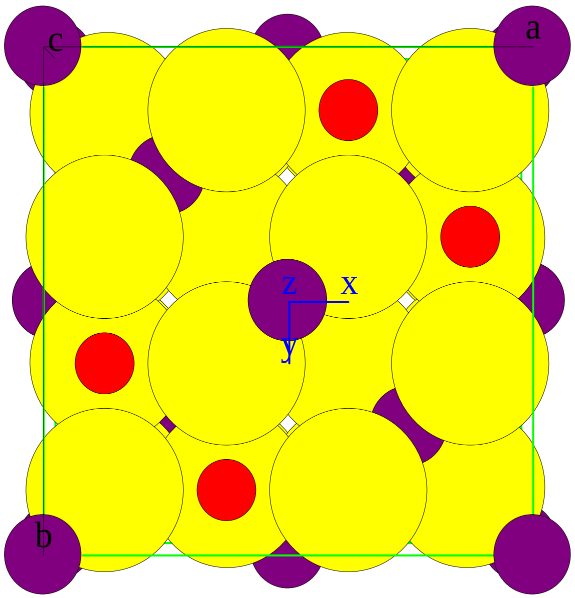
Mg : V
45 : 1

Component 1 - MgO under oxidation/reduction cycling



14V/VMgO – reduction in pure propane





Ordered overlayer is seen both in plan view (X) and in profile (Y)

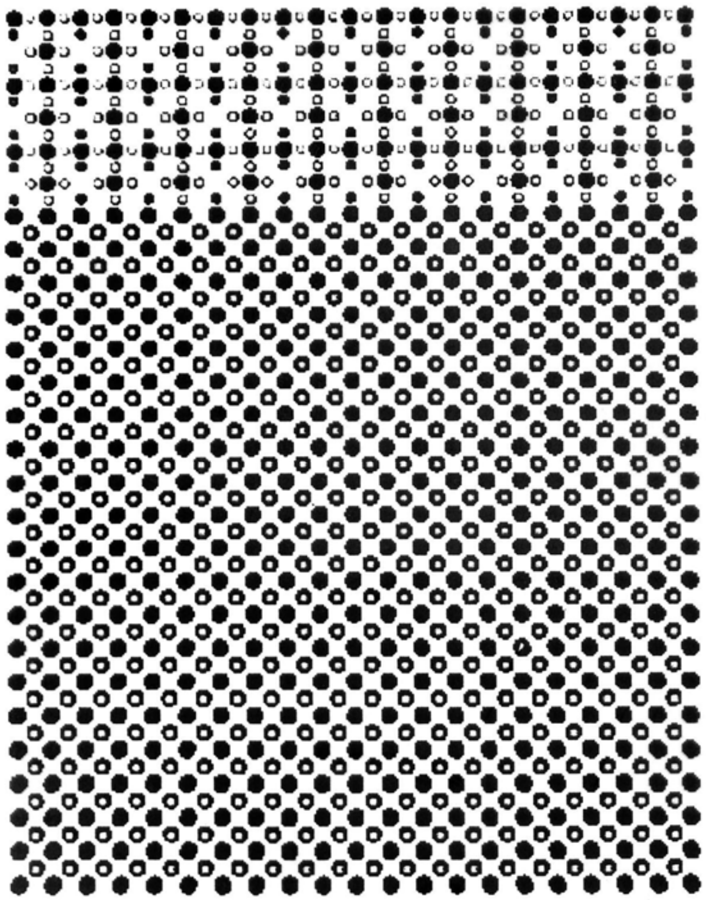
V^{3+} spinel phase

MgV_2O_4

a=0.843nm

Model A – Spinel layer

MgV_2O_4/MgO

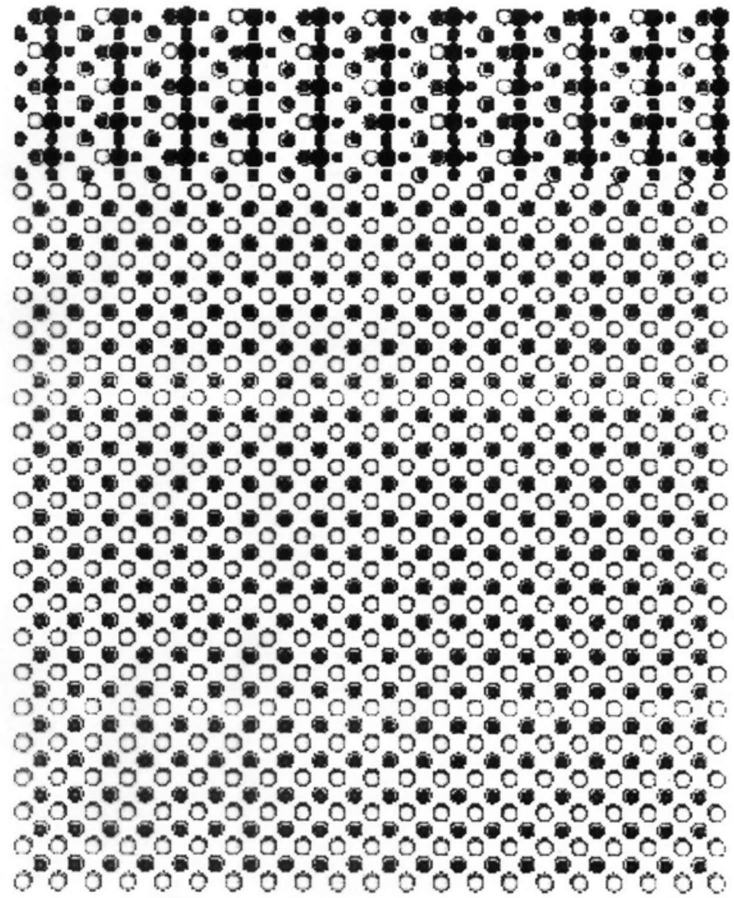


$MgO[100]//MgV_2O_4[100]$

$MgO[011]//MgV_2O_4[011]$

Model B – Ortho layer

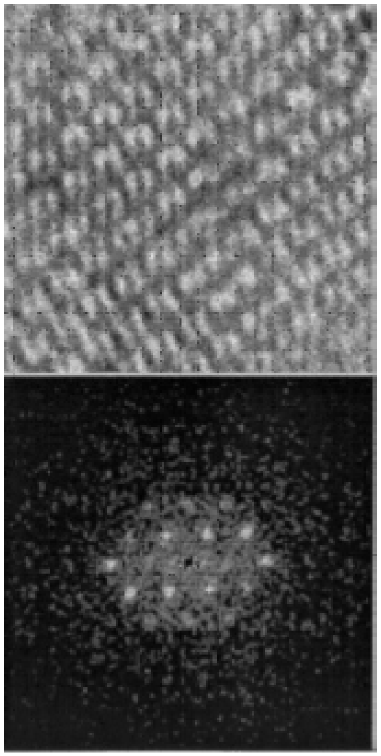
$Mg_3V_2O_8/MgO$



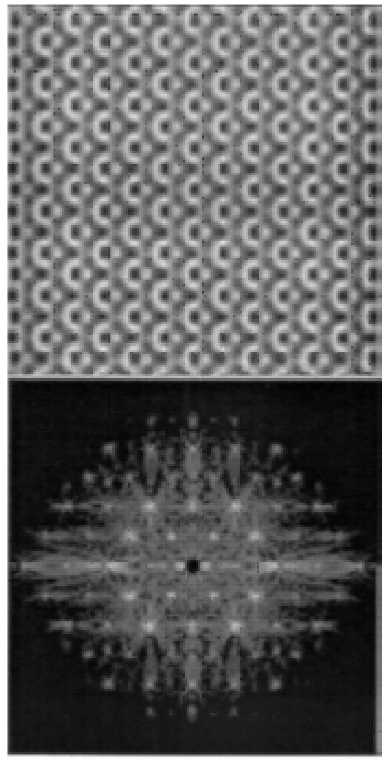
$MgO[100]//Mg_3V_2O_8[001]$

$MgO[011]//Mg_3V_2O_8[100]$

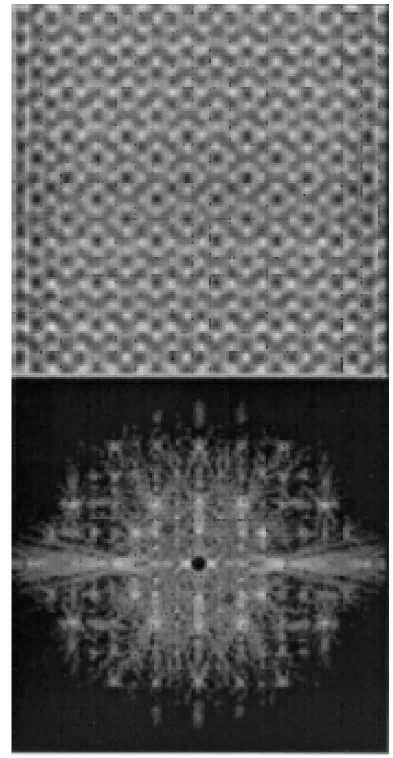
Comparing experimental HREM images with simulations from theoretical models



Experimental

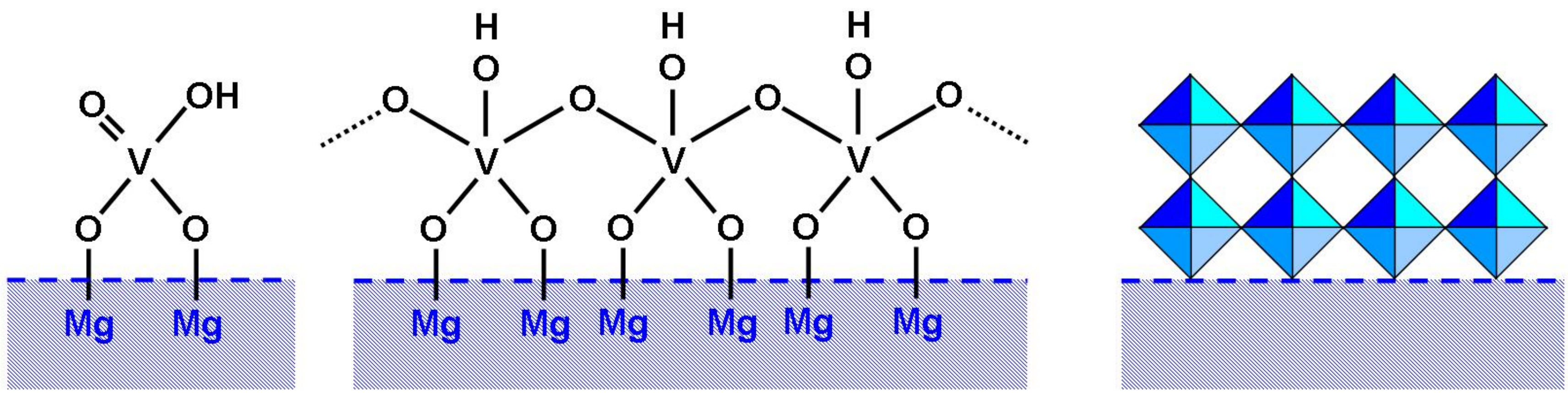


Spinel/MgO



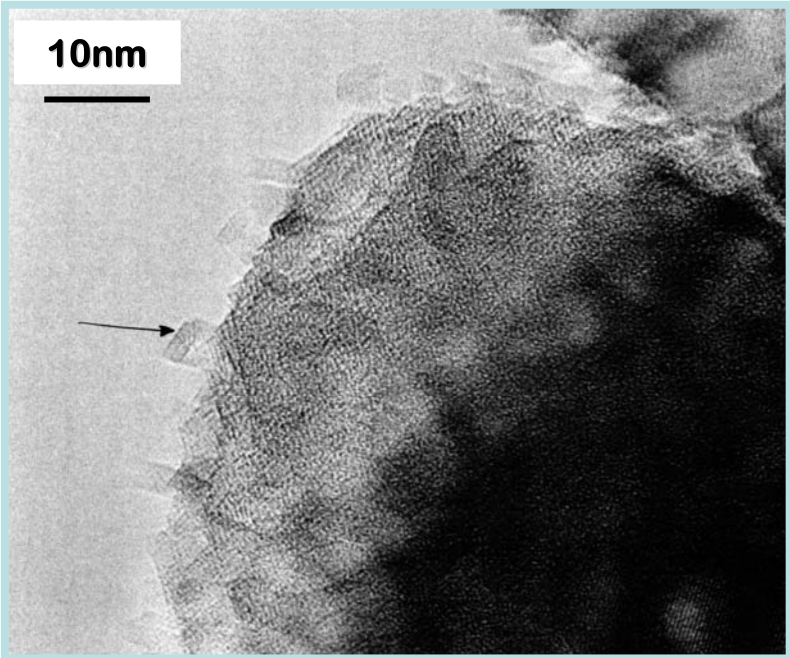
$Mg_3V_2O_8$/MgO

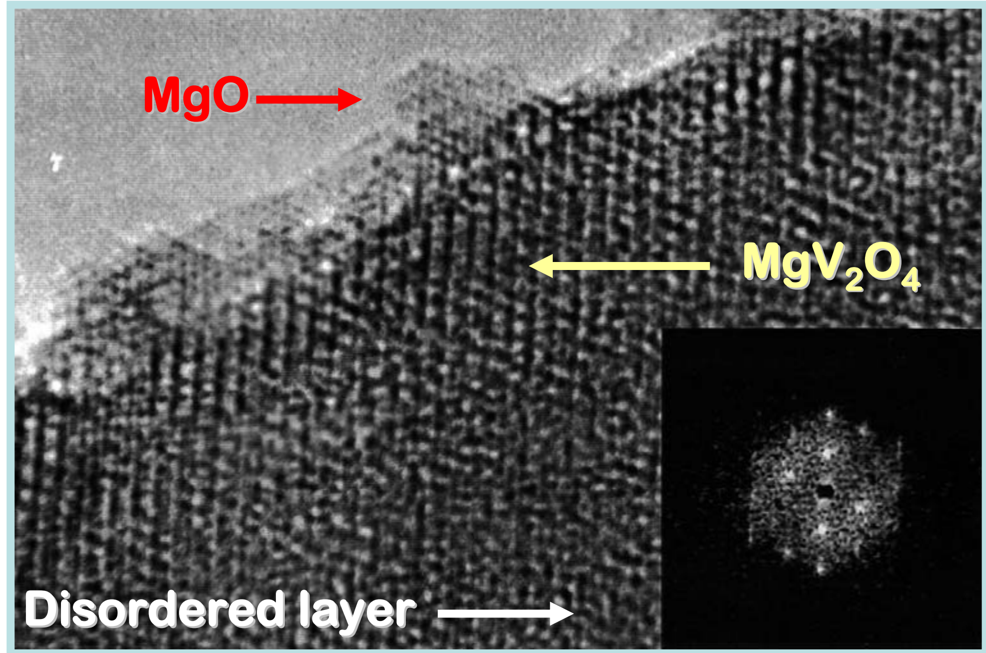
Component 1: Vanadium containing surface layer on MgO



isolated *polymeric* *crystal*

Component 2 - $Mg_3V_2O_8$ under reaction conditions





MgO crystallites on surface

MgV_2O_4 sub-surface layer

Disordered interior

$$Mg_3V_2O_8 \longrightarrow 2MgO + MgV_2O_4 + 2O$$

Reaction catalysed by lattice O atoms which are replenished from atmospheric oxygen (Mars van Krevelen mechanism)

14V/VMgO Catalyst

Component 1 – *film supported on MgO {111} platelets*

Disordered overlayer
V^{5+} / V^{4+}

Partially ordered overlayer
V^{3+}

MgV_2O_4/MgO epitaxial overlayer
V^{3+}

Component 2 – *bulk VMgO mixed oxide*

Crystalline $Mg_3V_2O_8$
V^{5+}

MgO/MgV_2O_4 on disordered interior
V^{3+}/V^{5+}

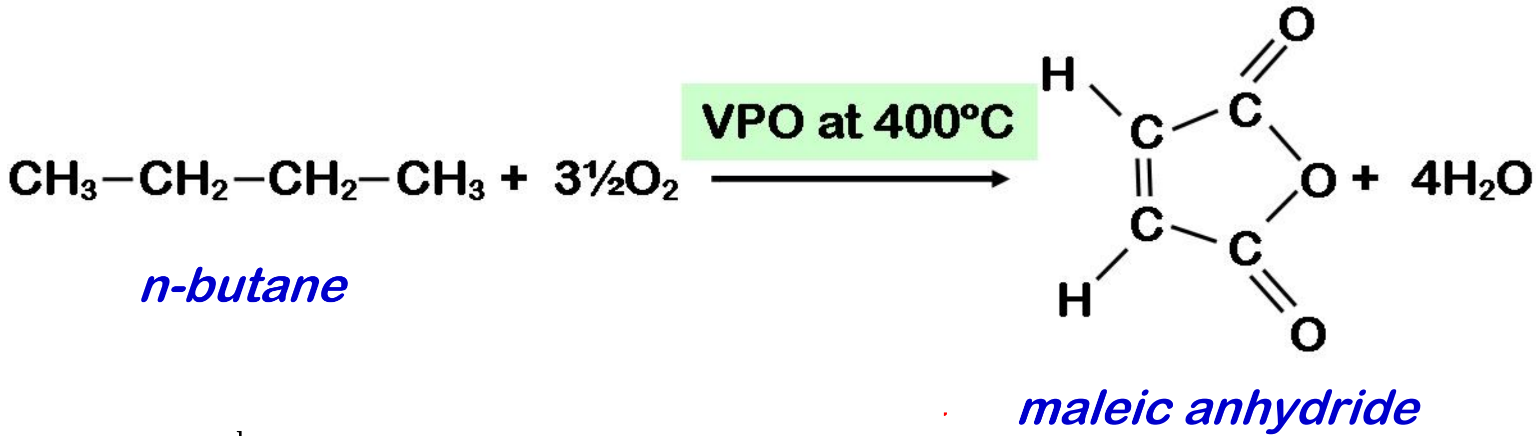
Crystalline MgV_2O_4
V^{3+}

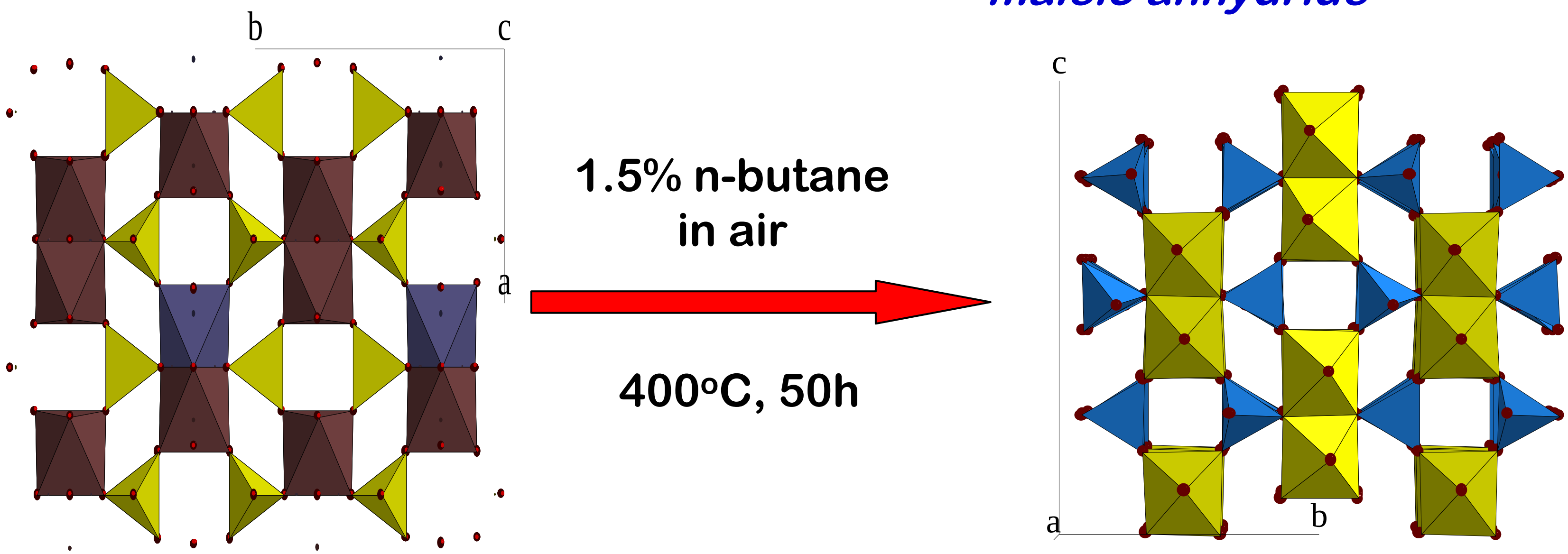
Oxidizing

Partially Reduced

Fully Reduced

Vanadium Phosphorus Oxide (VPO)

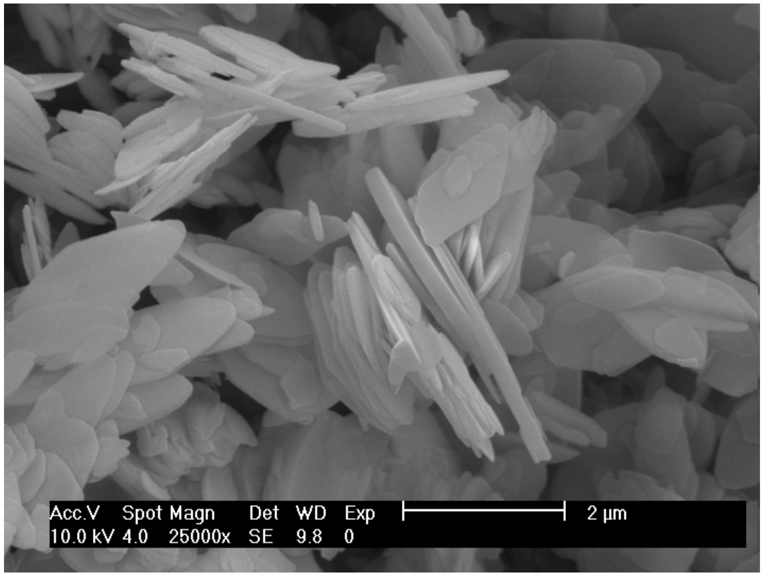


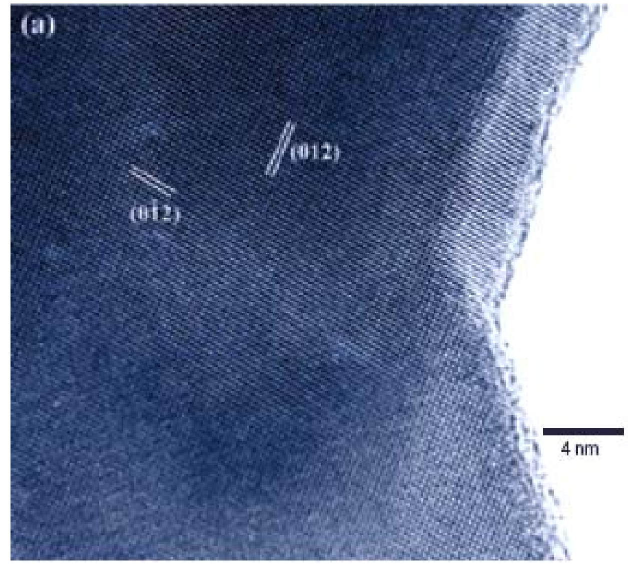


Vanadyl phosphate hemihydrate
$VOHPO_4 .0.5H_2O$

Vanadyl pyrophospate
$(VO)_2P_2O_7$

Does the VPO catalyst have a disordered surface layer?



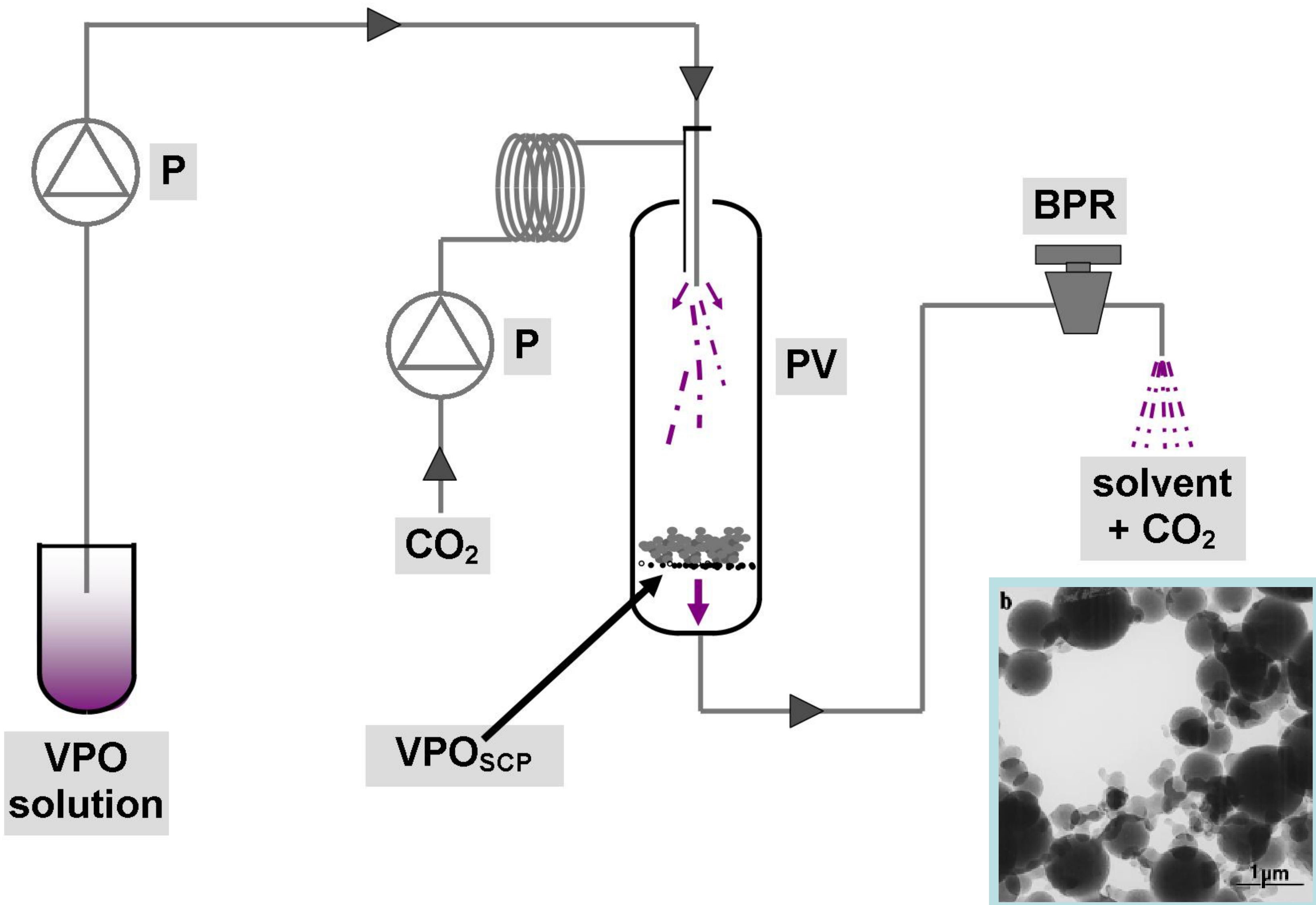


$(VO)_2P_2O_7$ platelets often show disordered surface layer
–is this a real effect or an artifact of beam damage?

XPS shows good catalysts to have:-

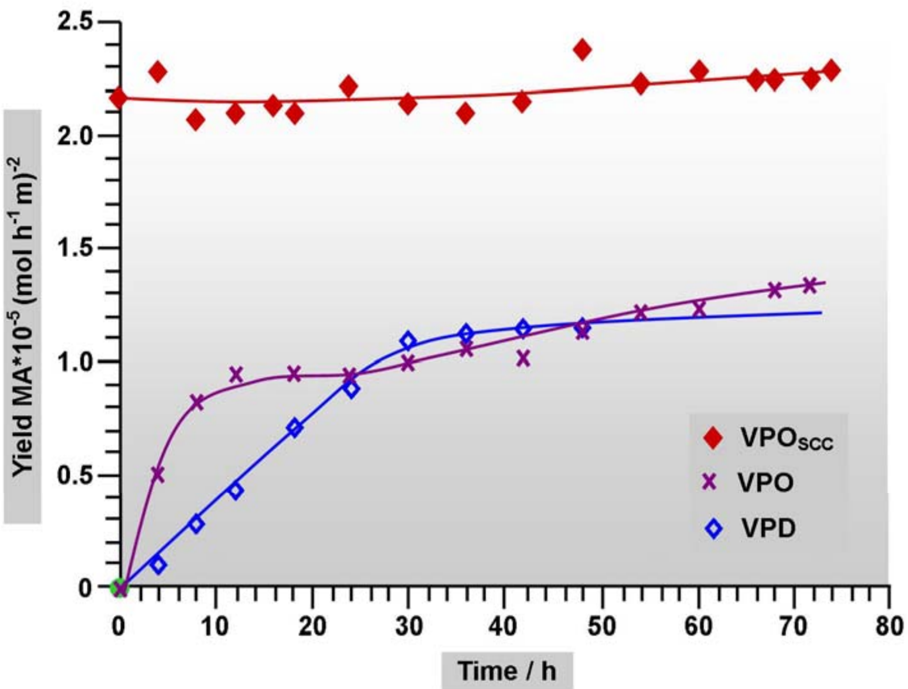
- a P/V ratio of 1.1 instead of 1.0 indicating a surface enrichment in P
- a mixture of V^{5+} and V^{4+} cations instead of only V^{4+}

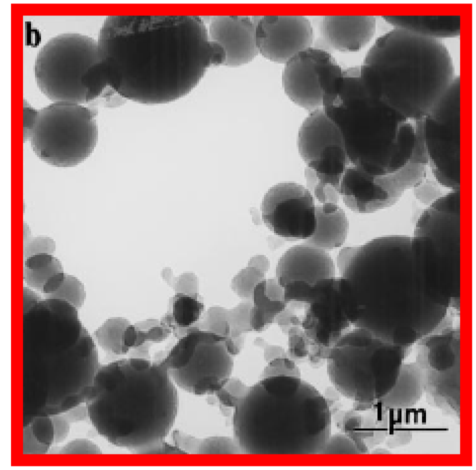
Amorphous Vanadium Phosphate Catalysts from Supercritical CO_2 Antisolvent Precipitation

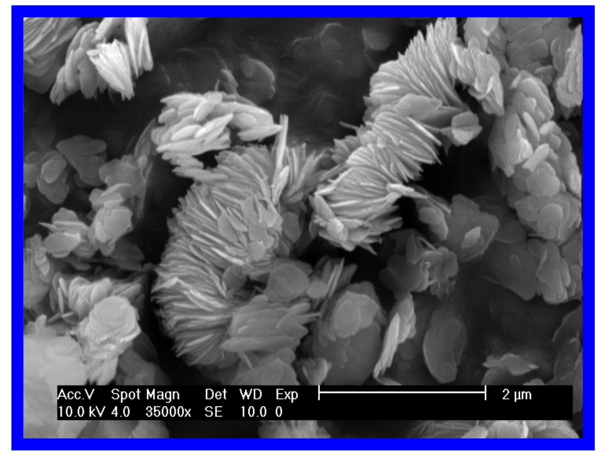


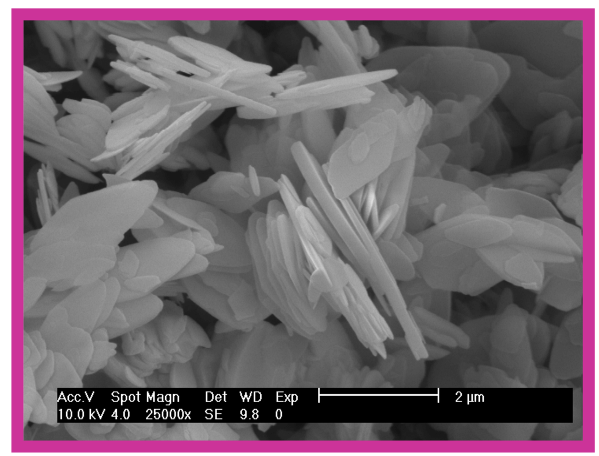
VPO – comparison of catalytic activities

Preparation Route	Conversion (%)	Selectivity (%)	Surface Area (m^2g^{-1})	Specific Activity (Mol MA $m^{-2}h^{-1}$)
VPO	27	52	14	1.35×10^{-5}
VPD	62	64	43	1.19×10^{-5}
VPO_{SCC}	24	48	6	2.20×10^{-5}



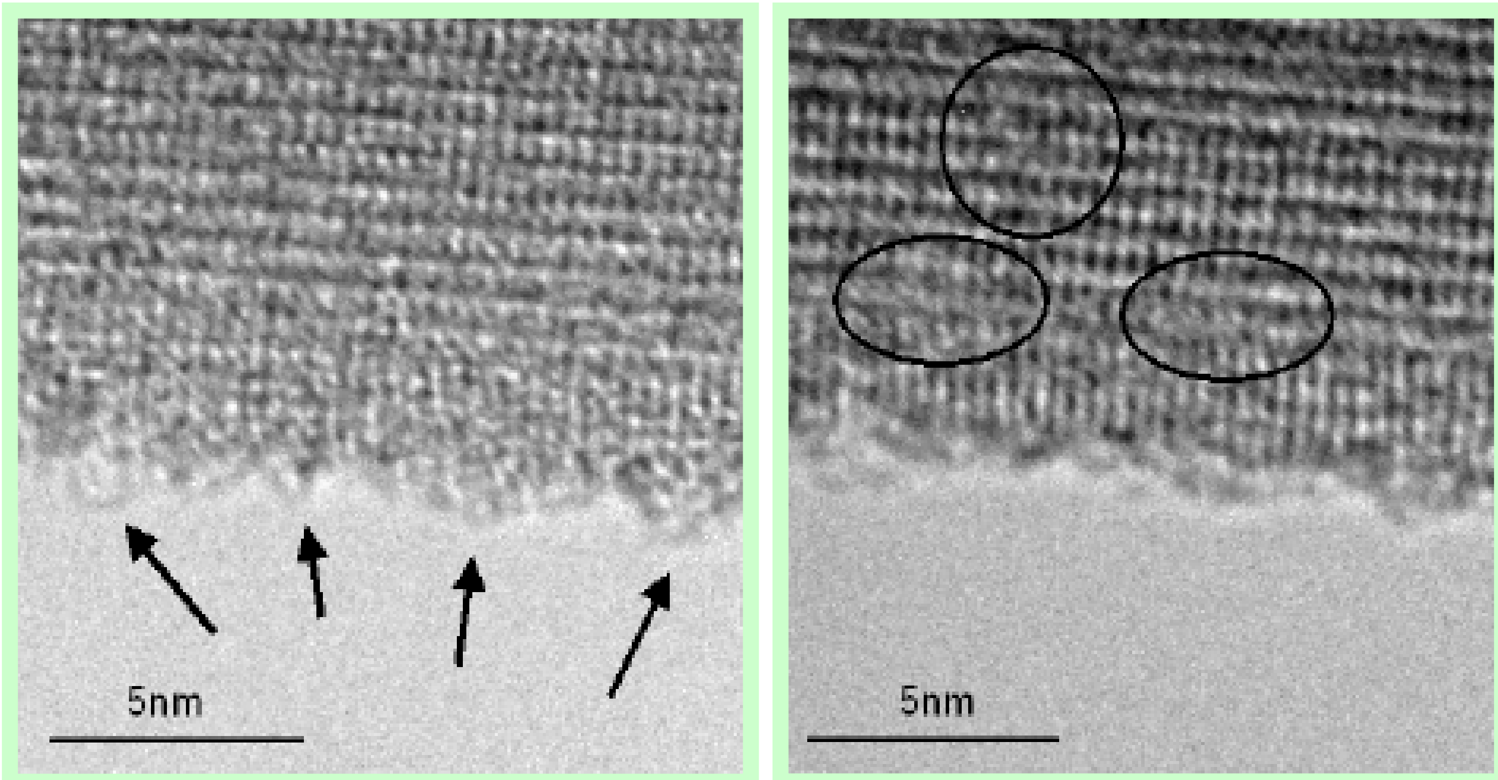






$MoBi_2O_6$ – surface disordered layers

- important catalyst for acrylonitrile and butadiene formation



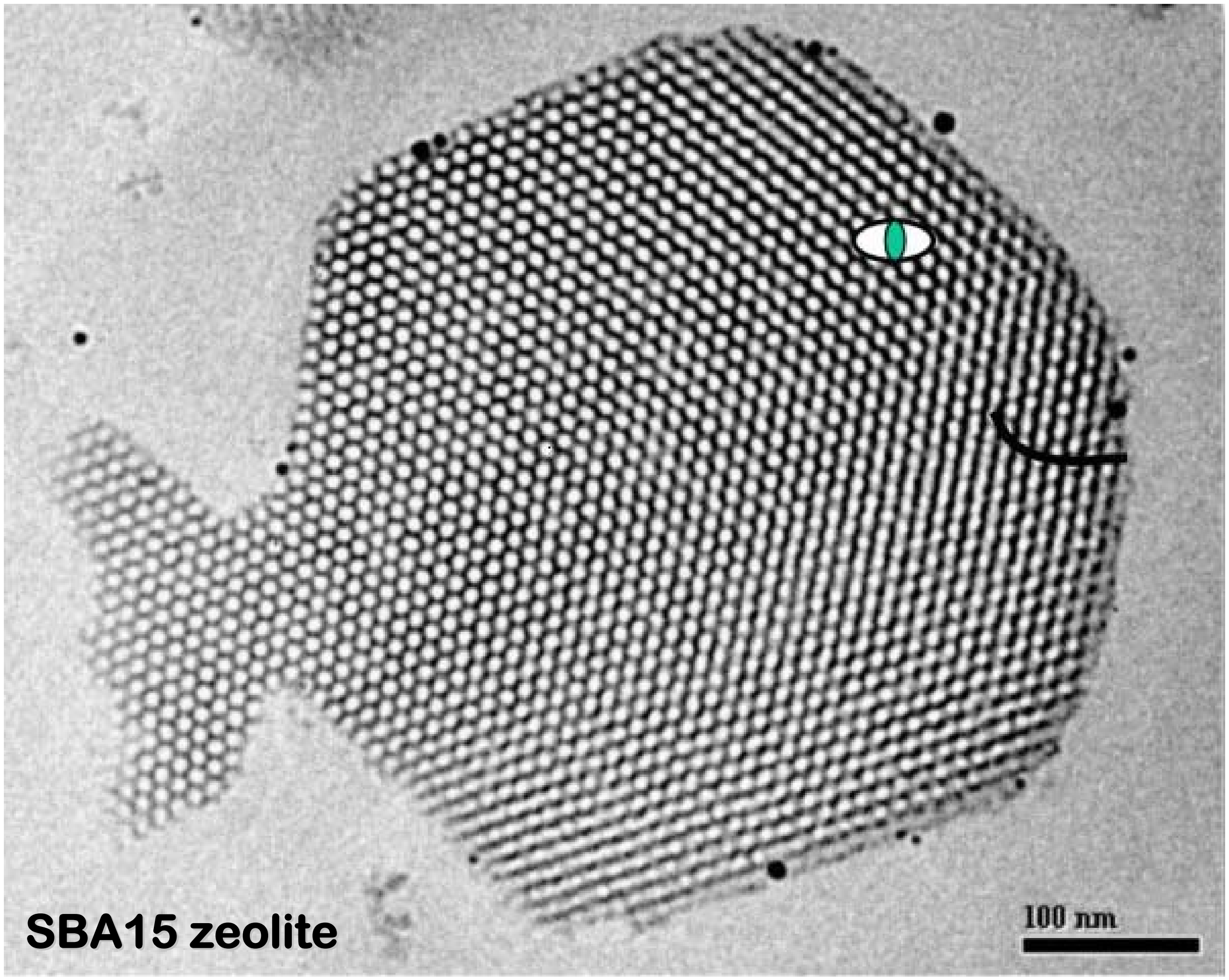
1-2nm thick disordered layer containing (by EELS) Mo, Bi and O

Conclusion

Reactant		Product	Catalyst
n-butane	→	maleic anhydride	VPO
propane	→	propene	VMgO
propene	→	acrolein	$FeSbO_4$
propene	→	acrylonitrile	$MoBi_2O_6$
butene	→	butadiene	$MoBi_2O_6$

It appears that a disordered surface layer is the active layer in these mixed oxide selective oxidation catalysts.

Zeolitic Nanofish



Courtesy Robert Schlogl – FHI, Berlin