

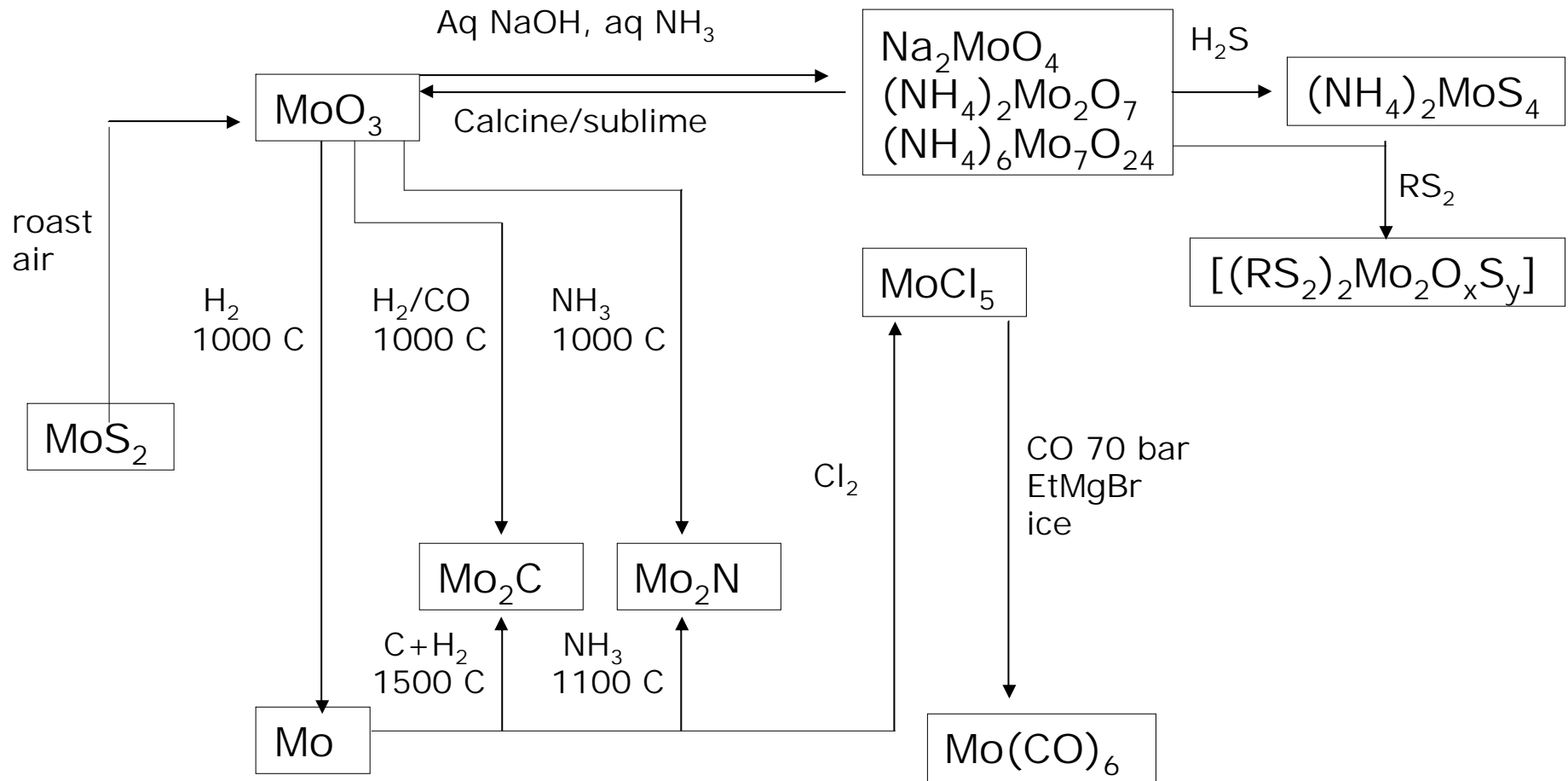
# Chemical Applications of Molybdenum

Understanding  
molybdenum chemistry  
and applications

Philip C.H. Mitchell  
School of Chemistry  
University of Reading  
Reading RG6 6AD UK

The purpose of the presentation is to show how technical applications of molybdenum compounds exploit fundamental molybdenum chemistry.

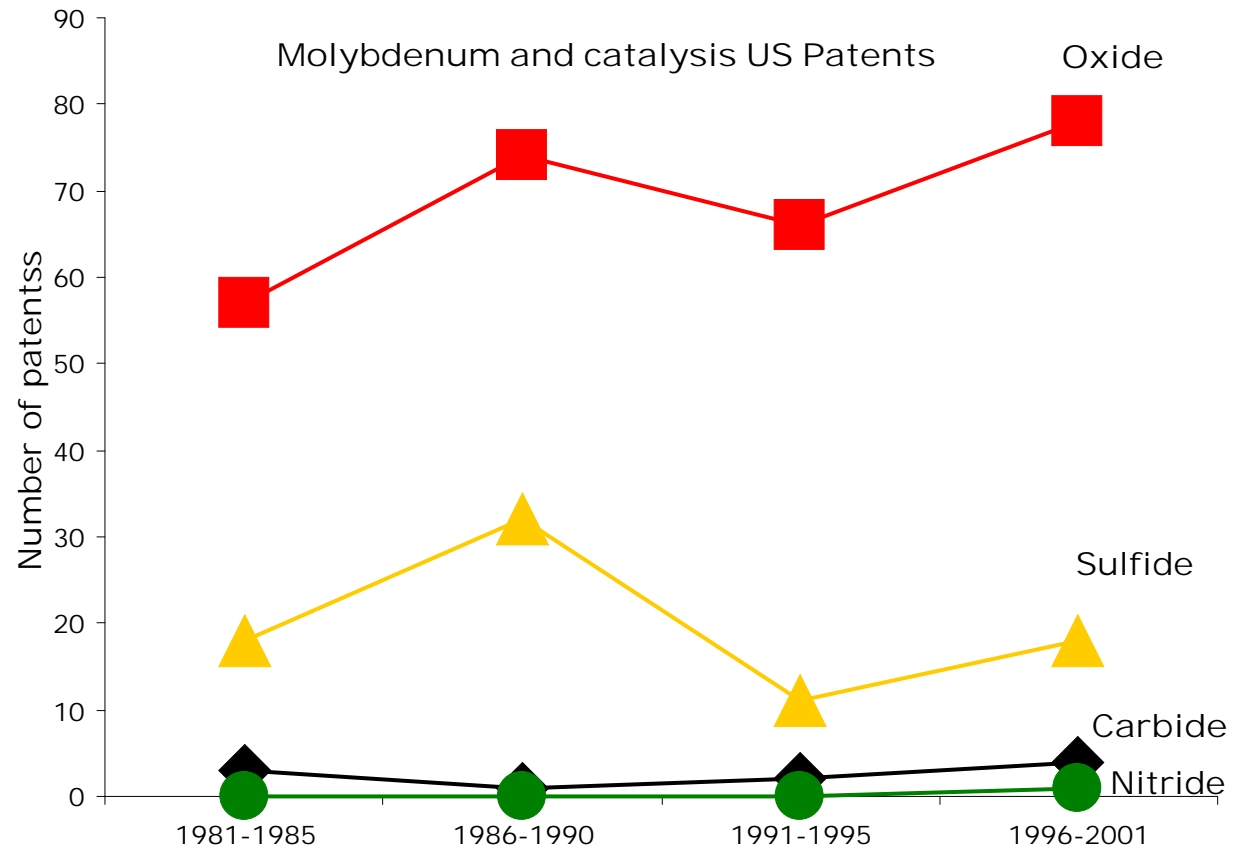
# Molybdenum Chemistry



# Molybdenum Compounds Applications

Application	Partner					
	C	N	O	Si	P	S
	Mo <sub>2</sub> C	Mo <sub>2</sub> N	MoO <sub>3</sub> molybdate	MoSi <sub>2</sub>	MoP	MoS <sub>2</sub>
Catalysis	☆	☆	★		☆	★
Lubrication						★
Corrosion inhibition			★			
Pigments			★			
Smoke suppression			★			
Ceramics				★		
Nanomaterials	☆					

# Molybdenum Catalysts US Patents



# Molybdenum Catalysts

Hydrotreatment of petroleum

Remove S = hydrodesulfurisation = HDS

Remove N, O compounds

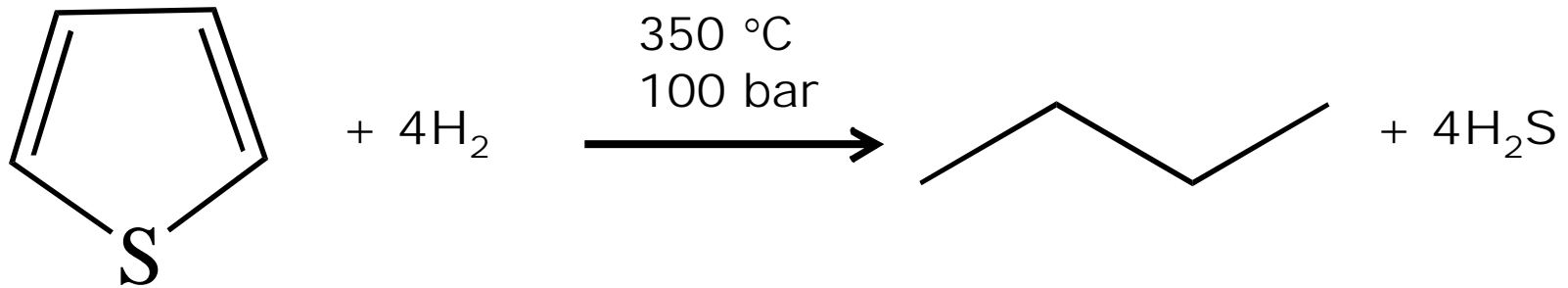
Selective oxidation

Methanol to formaldehyde

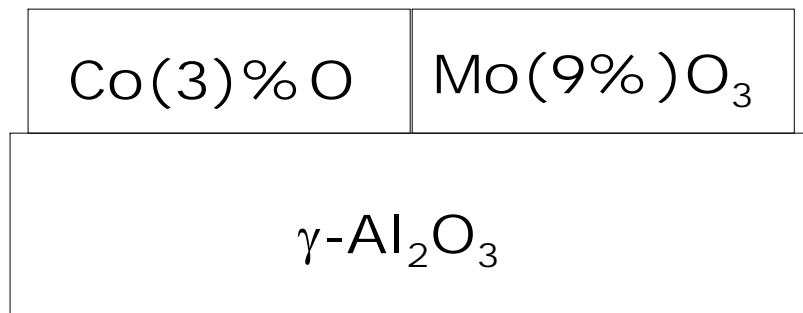
Propene to acrolein and acrylonitrile

For polymers and plastics

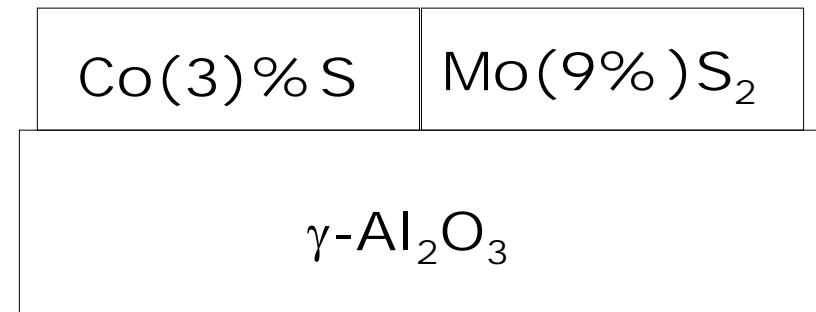
# Thiophene Desulfurisation



# Molybdenum Hydrodesulfurisation Catalyst



Pre-cursor  
Oxide form

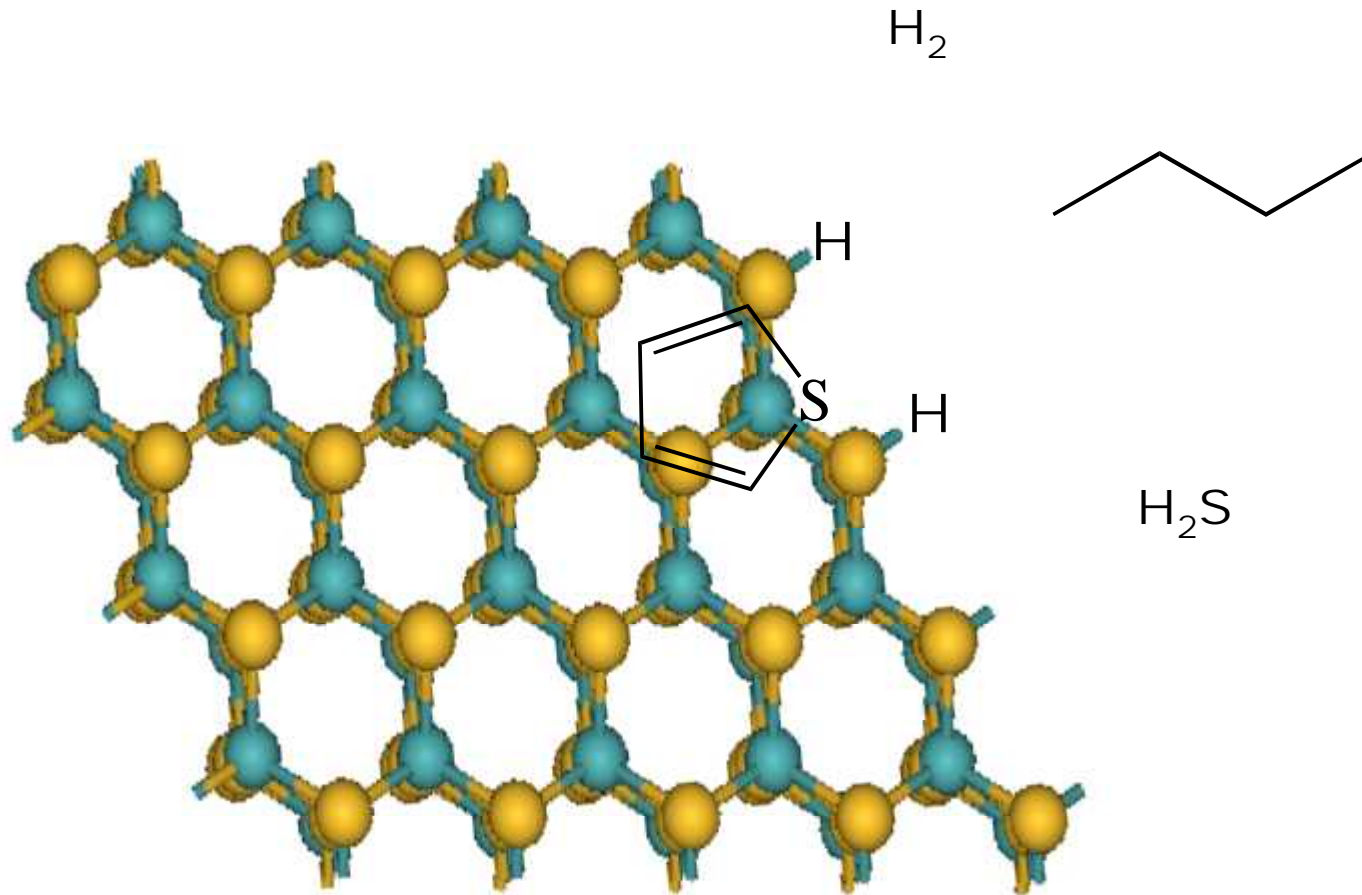


Active catalyst  
Sulfide



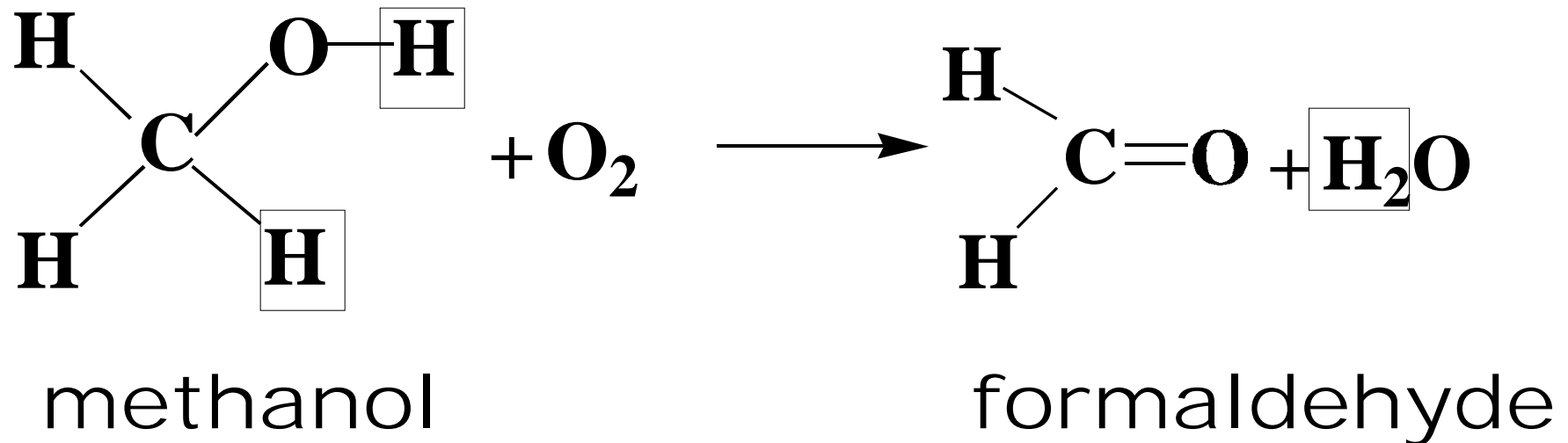
# MoS<sub>2</sub> Catalyst

## Thiophene Hydrodesulfurisation



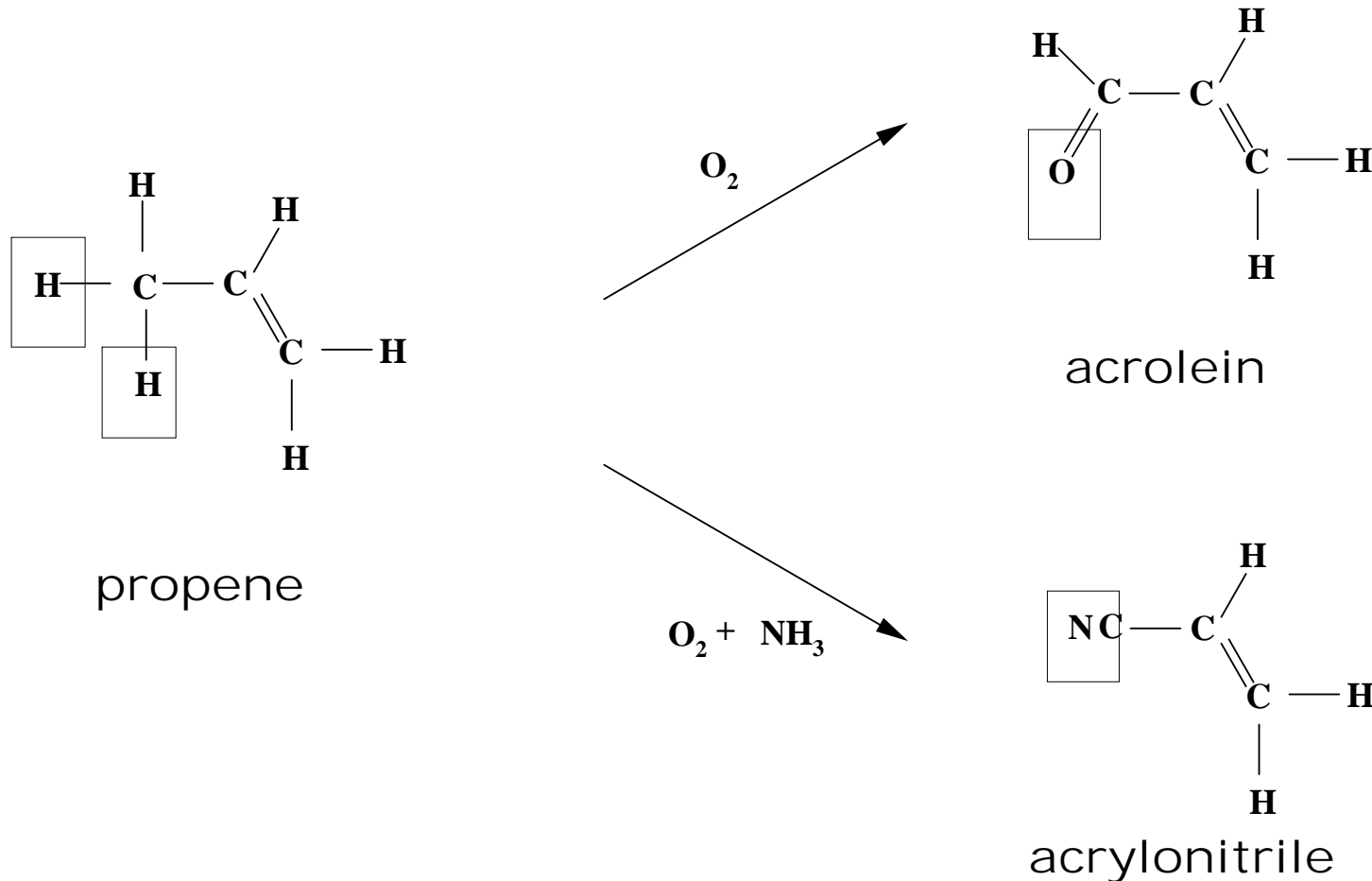
# Selective Oxidation Methanol

Iron molybdate  $\text{Fe}_2(\text{MoO}_4)_3$

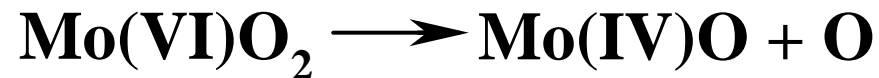
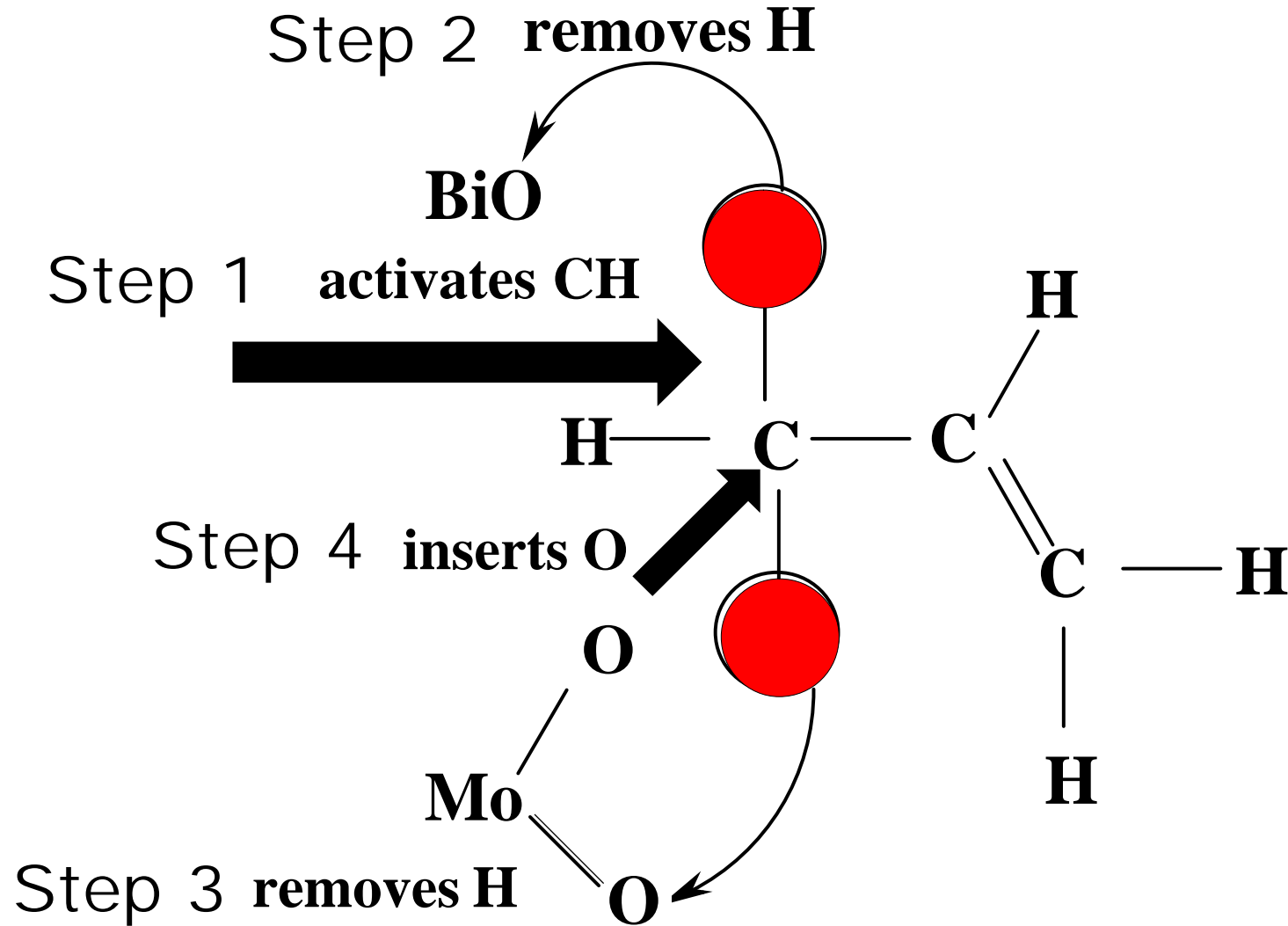


# Selective Oxidation of Propene

Bismuth molybdate  $\text{Bi}_2(\text{MoO}_4)_3$



# How Selective Oxidation Works



# Molybdenum sulfur Compounds in Lubrication

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## Molybdenum disulfide

Dry lubricant

Used in e.g.  
greases,  
dispersions,  
friction materials and  
bonded coatings.

## Molybdenum complexes

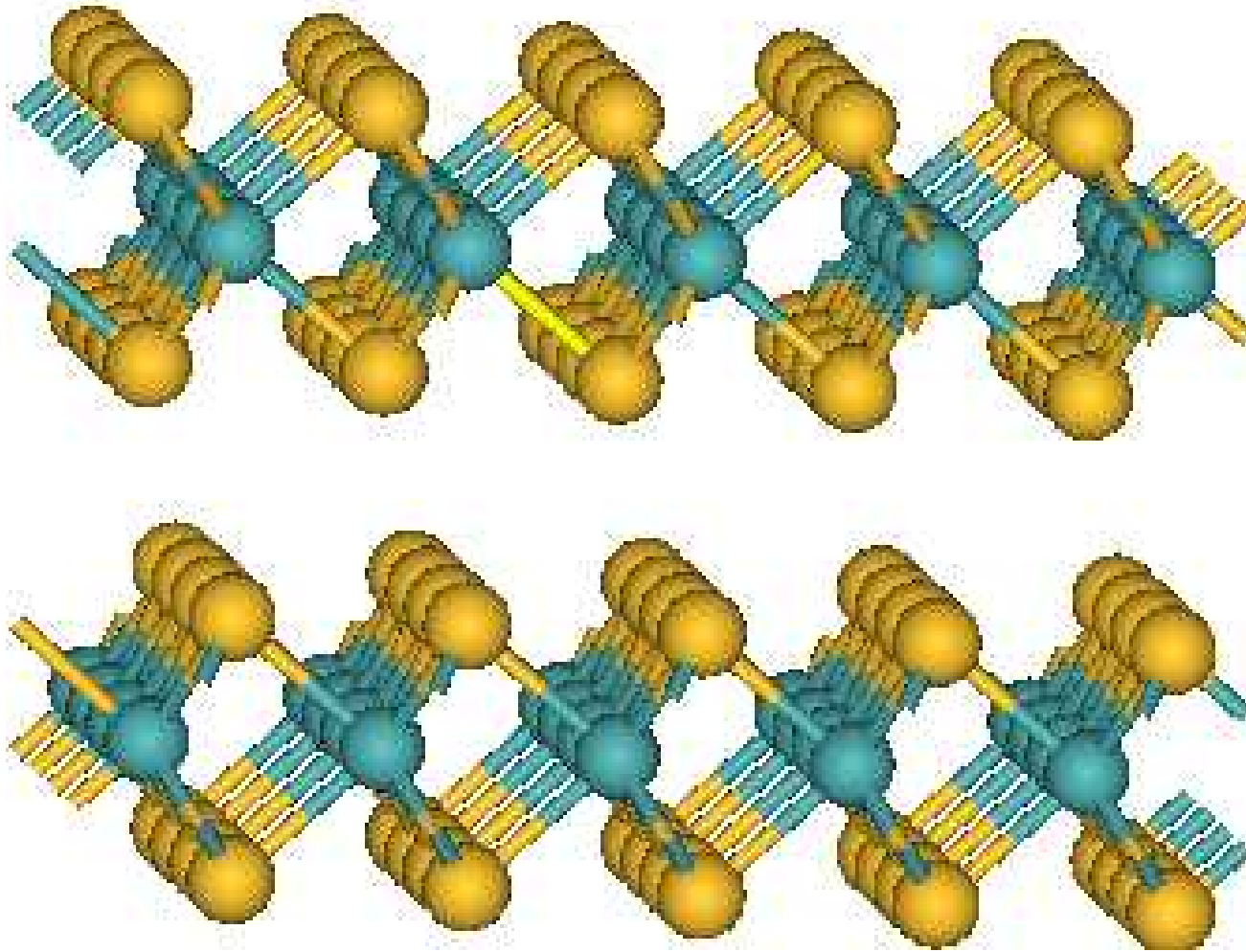
soluble in petroleum oils  
and other organic solvents

antiwear and  
extreme pressure additives

Decompose at  
hot metal surface  
Protective film  
MoS<sub>2</sub> layer

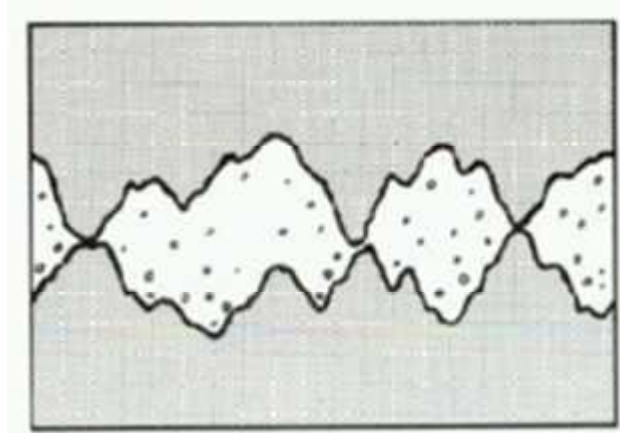
friction modifiers  
in lubricating oils and  
greases.

# MoS<sub>2</sub> Structure

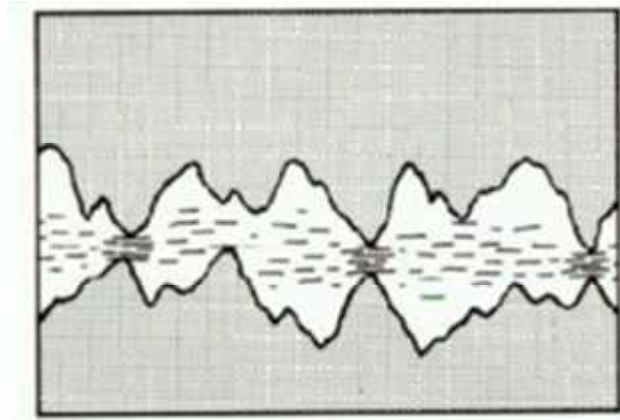


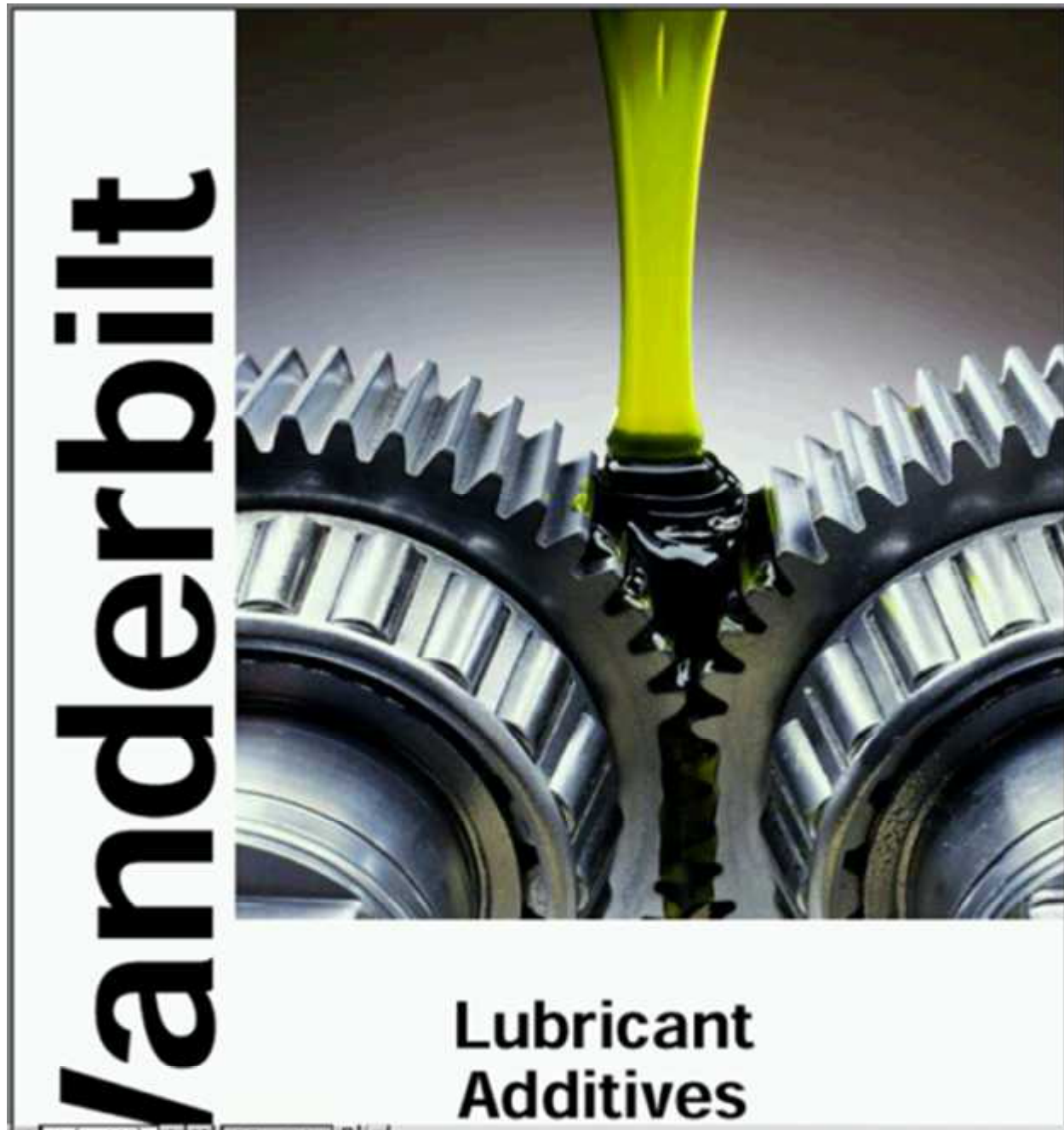
# MoS<sub>2</sub> Lubricating Action

No MoS<sub>2</sub>



With MoS<sub>2</sub>





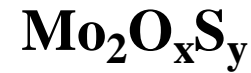
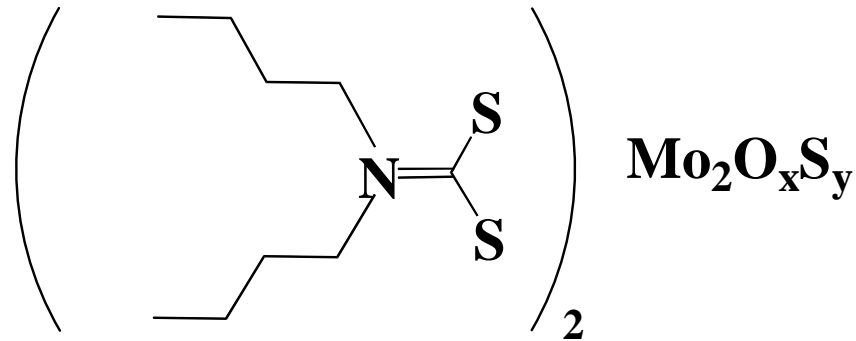
From R.T. Vanderbilt Company, Inc. Lubricants Information Brochure  
<http://www.rtvanderbilt.com/petro/p981.pdf>

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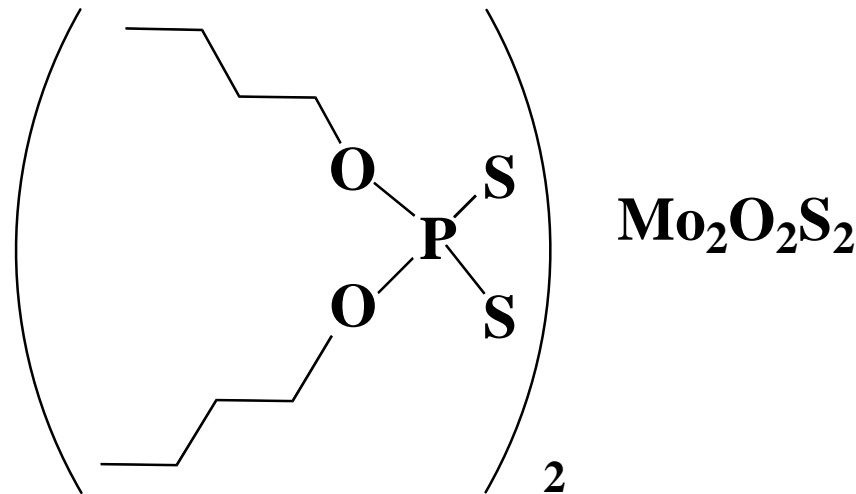


# Molybdenum Complexes

## Anti-friction, Anti-wear, Anti-oxidant



dithiocarbamate



dithiophosphate

# Corrosion Inhibitors and Pigments

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Replace toxic chromate by molybdate

Application	
Steel, Al, Cu	Sodium molybdate
Central heating systems	
Automobile engine coolant	
Paints plastics rubber ceramics	Zinc, calcium, strontium molybdate <b>Molybdenum orange: lead molybdate + lead chromate</b> <b>Phosphomolybdates</b>

# Calcium Zinc Phosphomolybdate<sup>19</sup> Corrosion Test



Reproduced with permission from *Paint and Coatings Industry* magazine 2001

Industry Update: Molybdate Corrosion Inhibitors

By Charles Simpson Moly-White Pigments Group, Cleveland, OH

<http://www.pcimag.com>.

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# Mechanism of Protective Action of Molybdate

Interacts with the metallic substrate adsorption.

Fills gaps and promotes the formation of an adherent oxide layer.

Prevents corrosion of the underlying substrate passivation.

# Molybdates as Smoke Suppressants

Non-volatile Mo oxide remains in char.

Application	Compound
PVC cable carpet backing building materials	Ammonium octamolybdate $\text{MoO}_3$

# Mechanism of Smoke Suppression by Molybdate

Plasticizers greatly enhance the polymer combustibility.

Molybdate reduces smoke from burning PVC.

The char produced from the AOM containing compound was  $\text{MoO}_2$ .

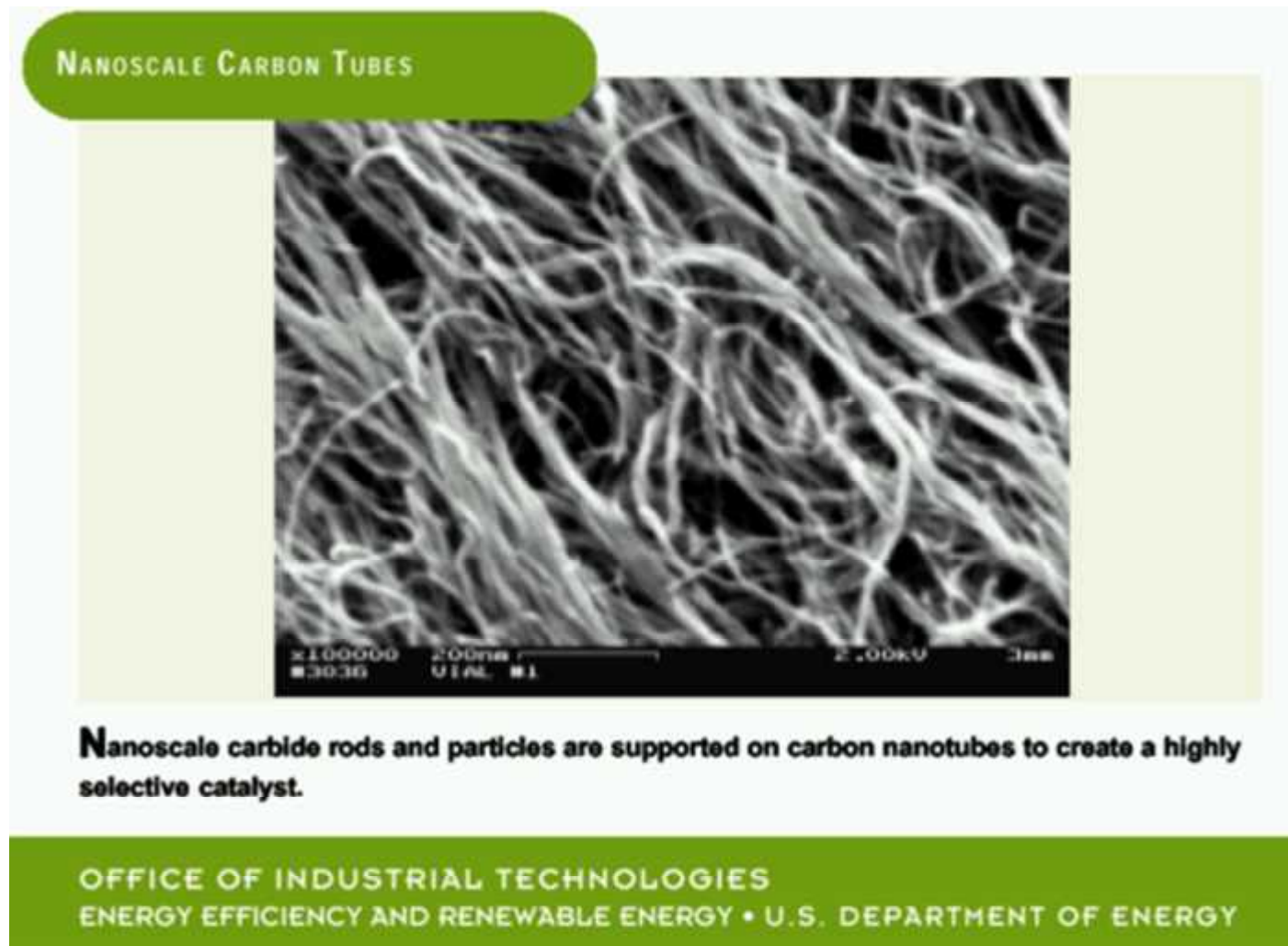
Cross-links the plastic to form a surface char..

# Molybdenum Disilicides

## Ceramics, advanced materials, composites

Application	Properties
<b>Heating elements air furnaces</b>	<ul style="list-style-type: none"> <li>• High melting point 2030 C</li> <li>• Moderate density 6.24 g cm<sup>-3</sup></li> <li>• Excellent oxidation resistance</li> </ul>
<b>Gas burner</b>	
<b>Diesel engine glow plugs</b>	
<b>Molten metal lances</b>	
<b>Aerospace gas turbine engines blade outer seal</b>	

# Molybdenum Carbide Catalyst Nanotubes



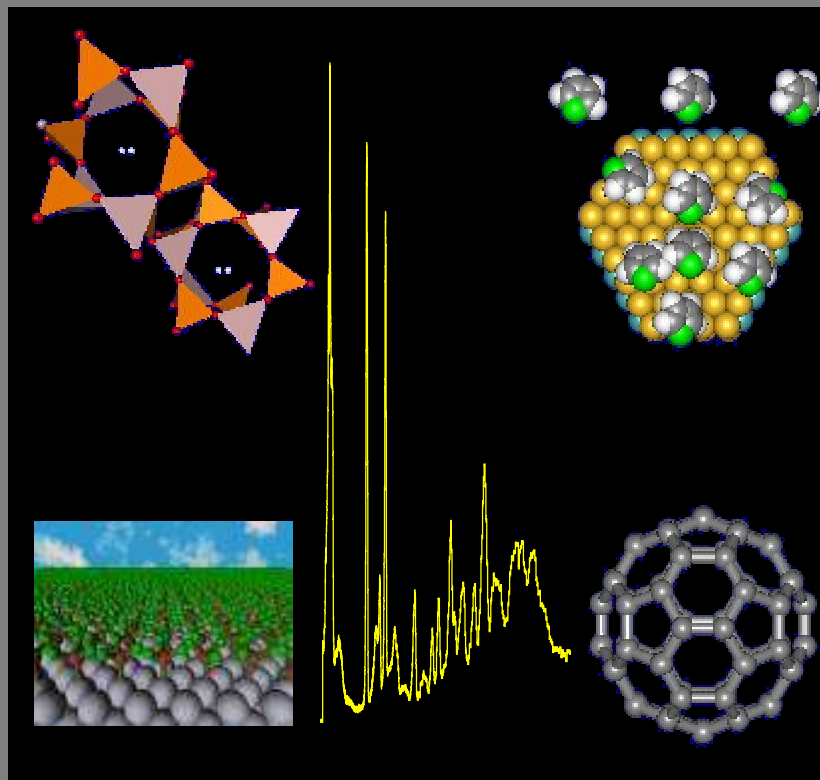
From U.S. Department of Energy 2002  
<http://www.oit.doe.gov/chemicals/factsheets/nanoscale.pdf>

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# Vibrational Spectroscopy with Neutrons

## With Applications in Chemistry, Biology, Materials Science and Catalysis

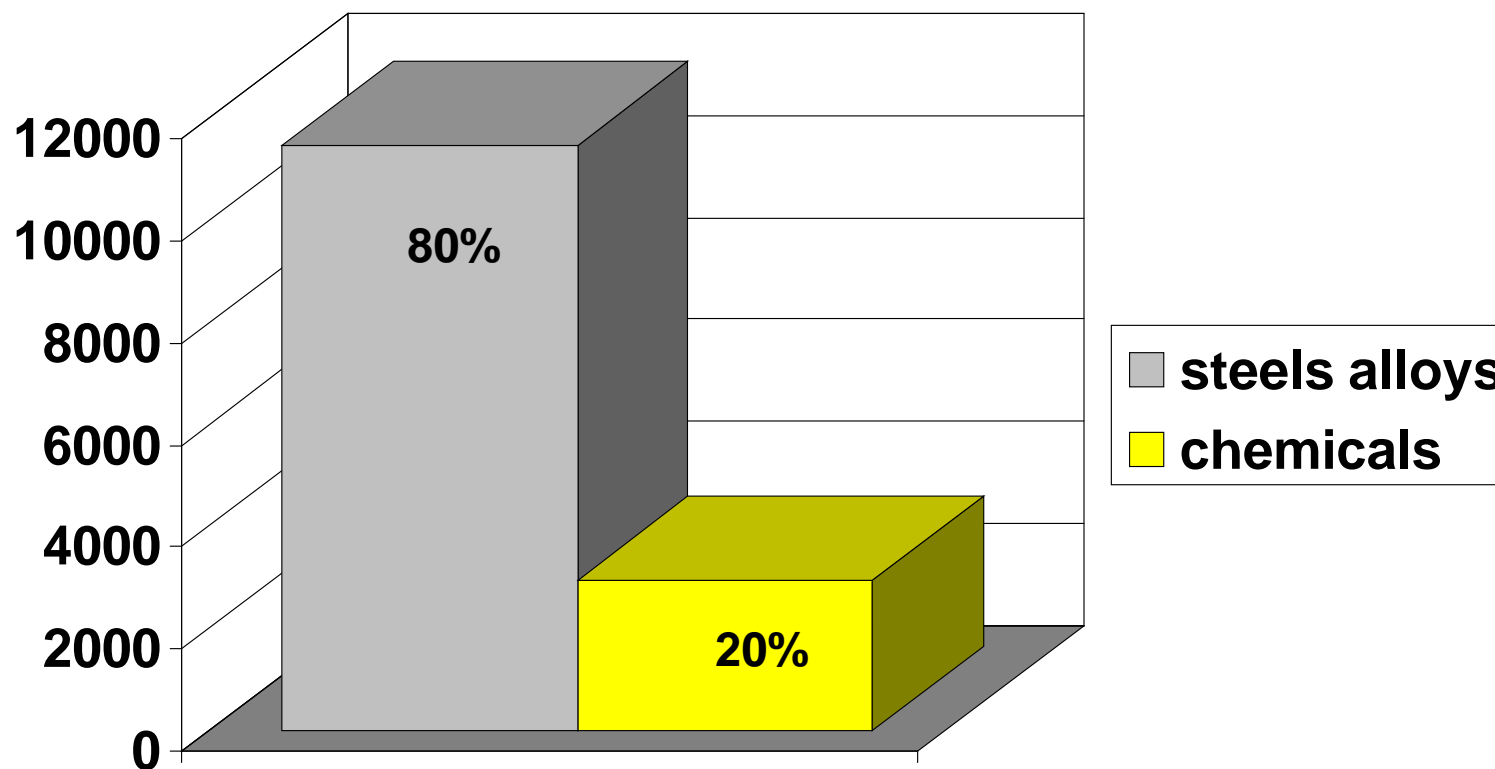


PCH Mitchell, SF Parker,  
AJ Ramirez-Cuesta and J Tomkinson

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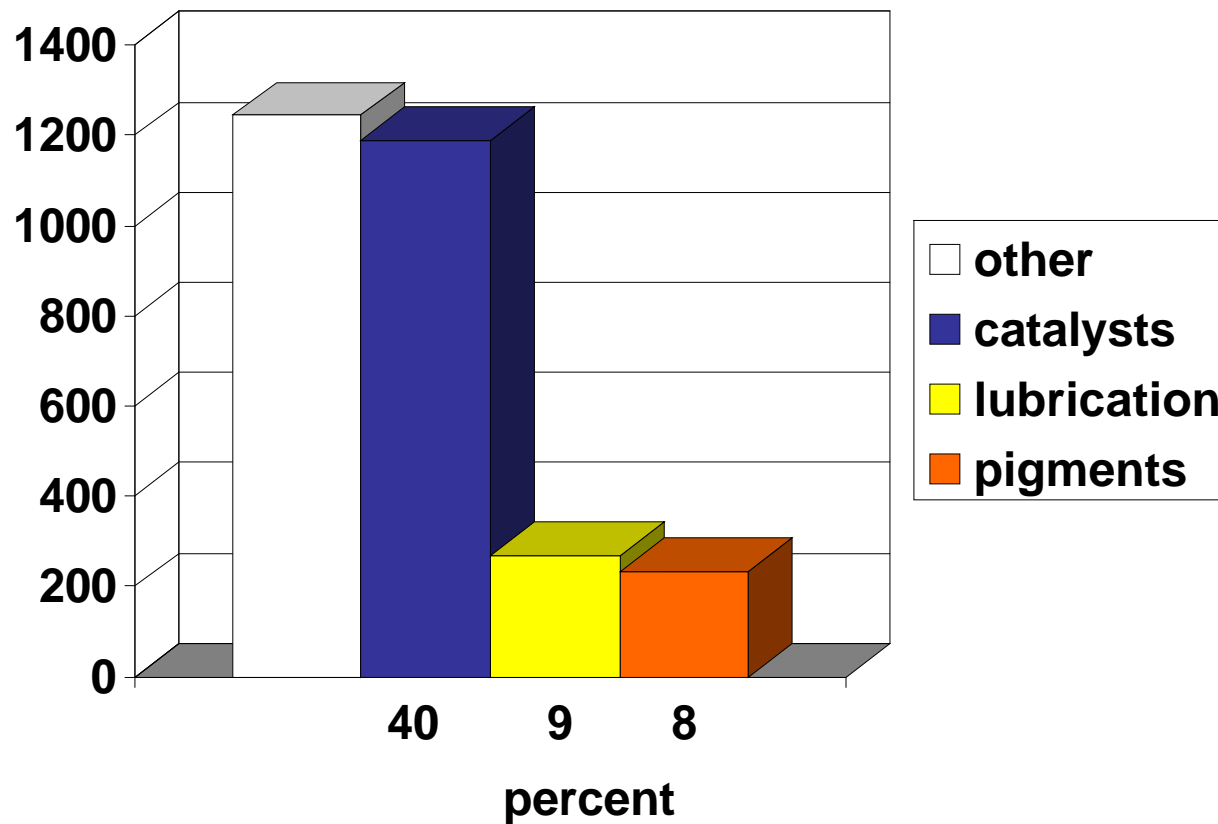
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# Molybdenum Usage United States 2002 metric tonnes



# Molybdenum Chemicals Usage United States 2002 metric tonnes

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*US Geological Survey Minerals Division*

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# Challenges 1

## Discovery

Applications	Mo compounds	
	old	new
old		
new	The hydrogen economy	

# Challenges 2

## Substitution

Catalysts	Vanadium? Iron?
Lubrication	Ashless additives to eliminate sulfur, phosphorus and ash
Pigments and coatings	Organics?

# Optimism

## U.S. Geological Survey Mineral Commodity Summaries

January 2004

The variety of uses for molybdenum materials, few of which afford acceptable substitution, has resulted in a doubling of demand in the Western World to about 136,000 metric tons per year (t/yr) (300 million pounds per year) in 2000 from about 68,000 t/yr (150 million pounds per year) in 1983.

# WHY USE MOLYBDENUM?

**Chemical versatility**

Low toxicity

ALWAYS WORTH THINKING  
MOLYBDENUM

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