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Characterization of solid catalysts

2. TPR and TPO

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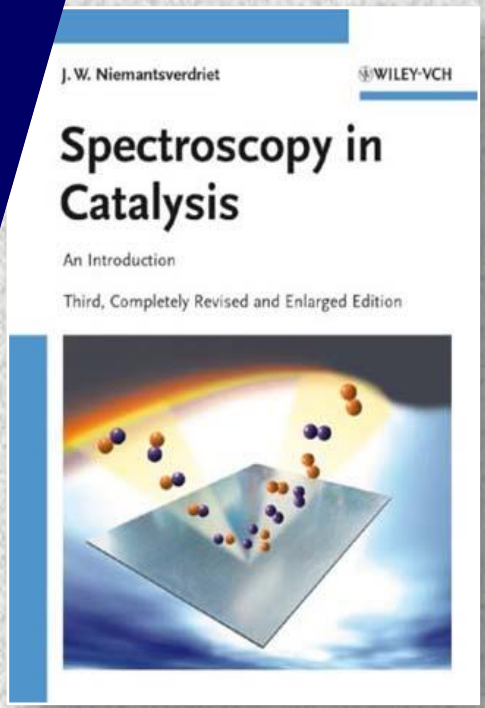

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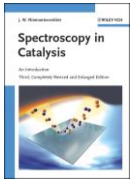
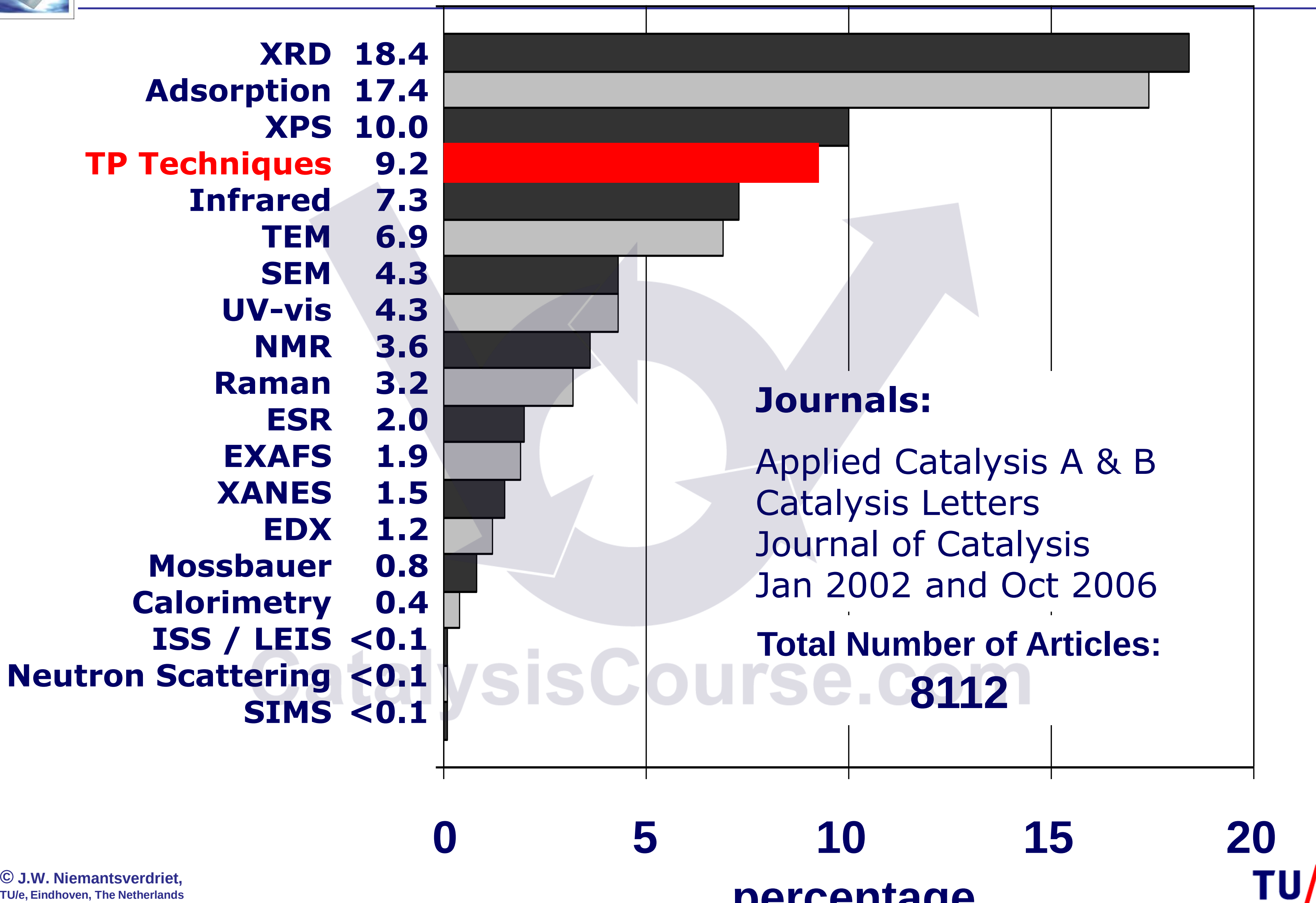
Where innovation starts



How often are techniques used



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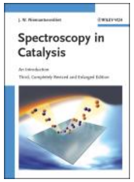
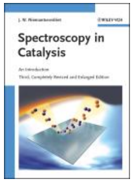


Temperature Programmed Techniques

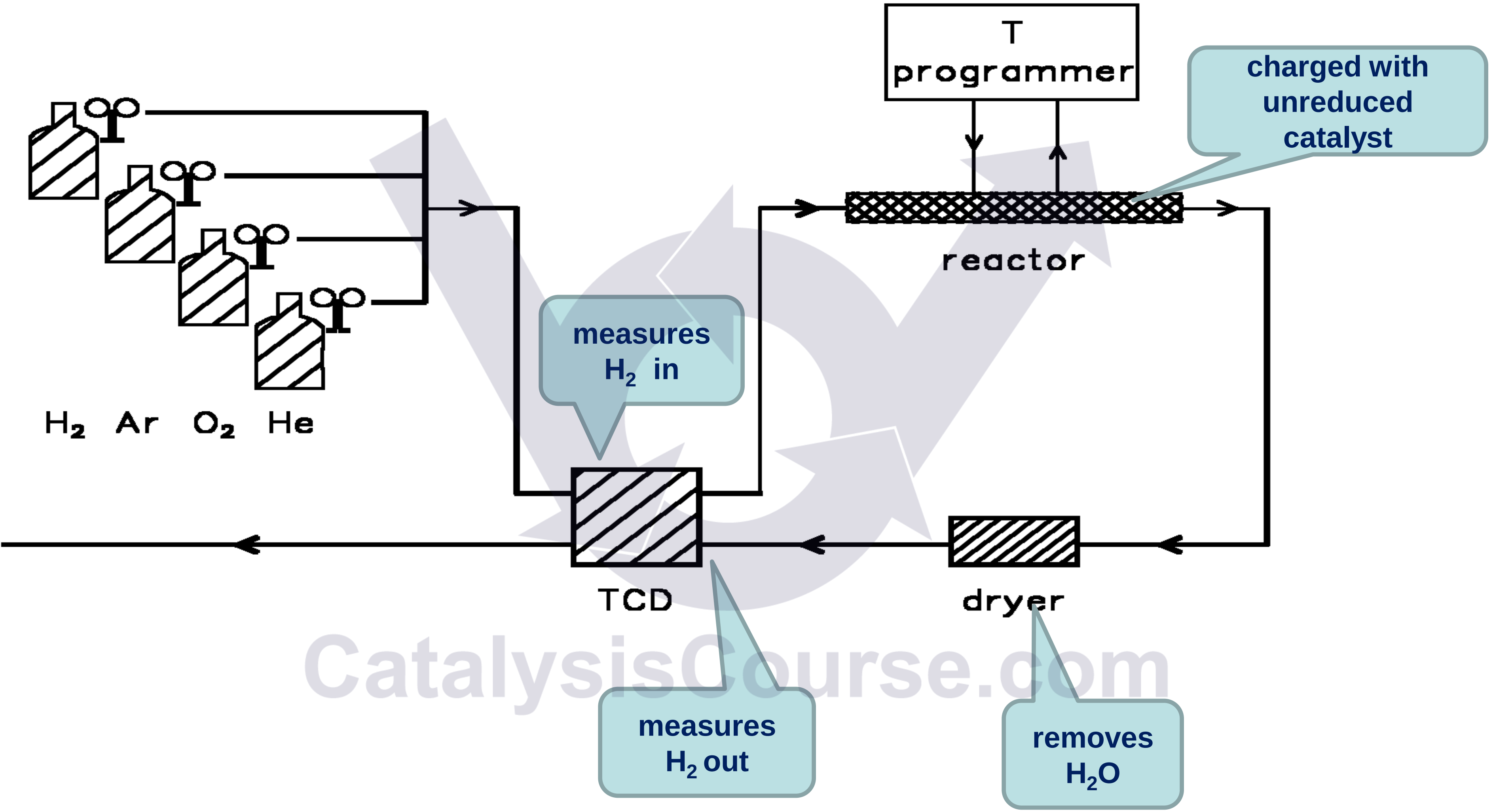
TPR	Reduction
TPO	Oxidation
TPS	Sulfidation
TPD	Desorption
TPRS	Reaction Spectroscopy

TP-SIMS, TP-IR, etc



TPR set up

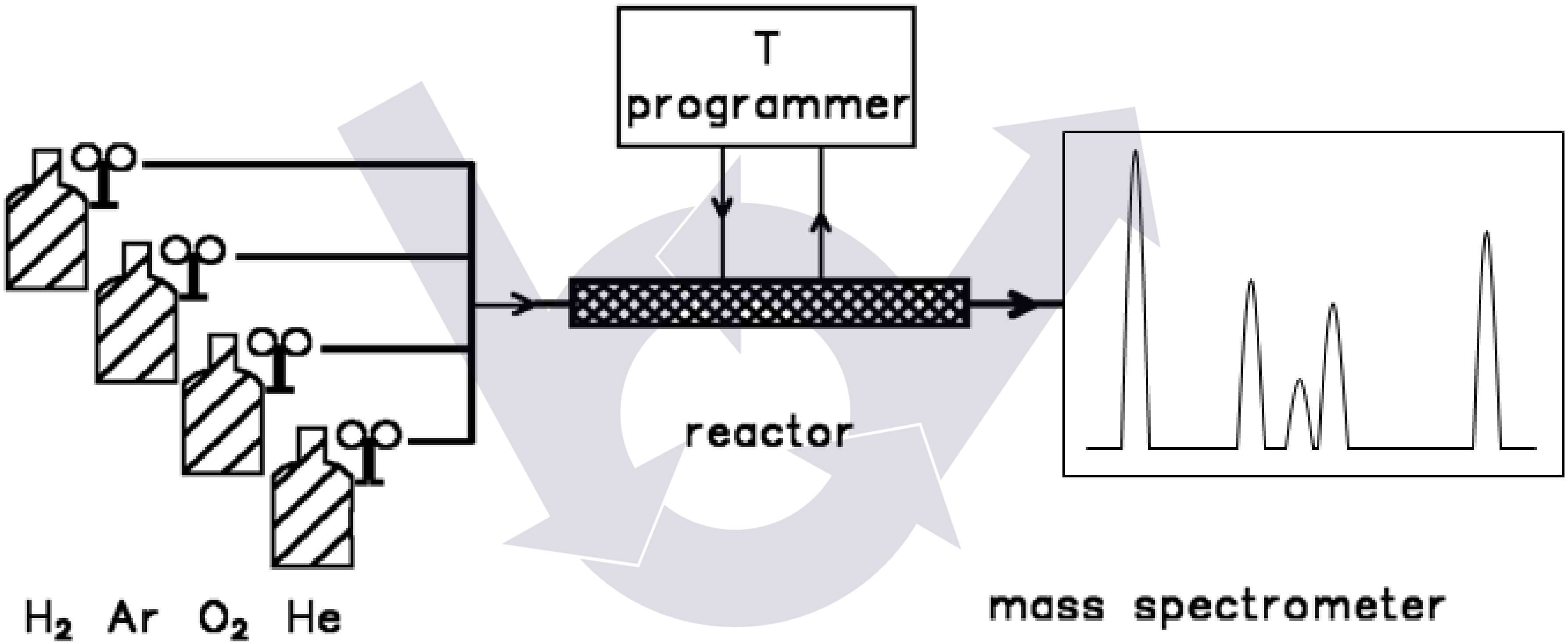
(based on thermal conductivity detector)



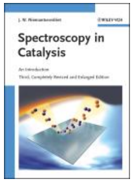
measures H_2 consumption by the catalyst as a function of temperature

TPR set up

(based on mass spectrometer)



mass spectrometer measures composition of the gas leaving the reactor as a function of temperature



Thermodynamics of Reduction

$$MO_n + nH_2 \rightarrow M + n\,H_2O$$

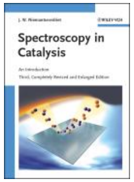
$$\Delta G = \Delta G^o + n\,RT\ \ln\left(\frac{p_{H_2O}}{p_{H_2}}\right)$$

$$\Delta G = n\,RT\ \ln\left[\left(\frac{p_{H_2O}}{p_{H_2}}\right) / \left(\frac{p_{H_2O}}{p_{H_2}}\right)_{eq}\right]$$

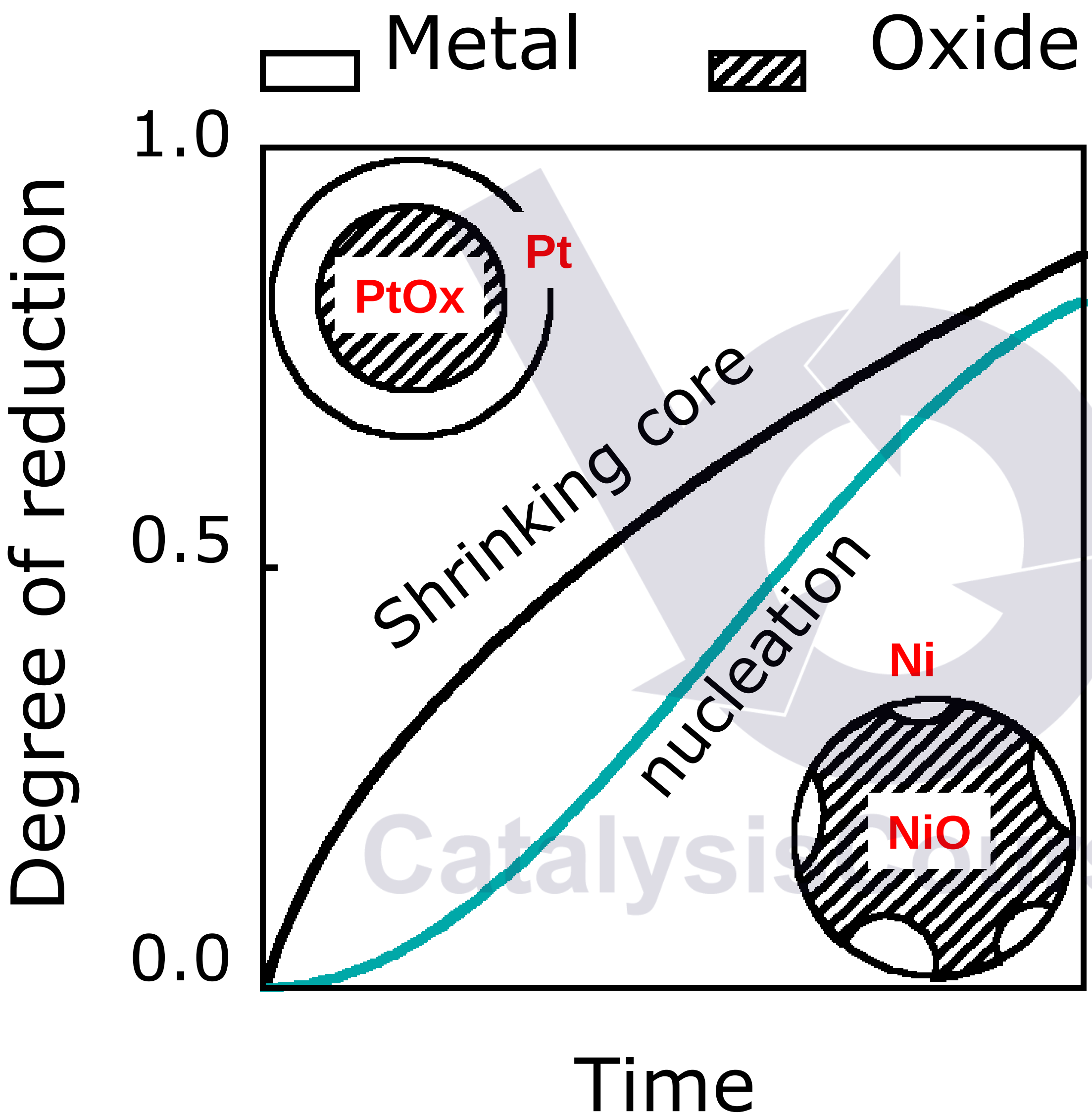
Metal	Oxide	$(p(H_2O)/p(H_2))_{eq}$
Ti	TiO_2	$4 \cdot 10^{-16}$
	TiO	$2 \cdot 10^{-19}$
V	V_2O_5	$6 \cdot 10^{-4}$
	VO	$2 \cdot 10^{-11}$
Fe	**Fe_2O_3**	**0.7**
	FeO	**0.1**
Co	CoO	50
Ni	NiO	500
Cu	CuO	$2 \cdot 10^{8}$
	Cu_2O	$2 \cdot 10^{6}$
Mo	MoO_3	40
	MoO_2	0.02
Rh	**RhO**	**10^{13}**
Pd	PdO	10^{14}
Ag	Ag_2O	$3 \cdot 10^{17}$

at 400 °C

Careful removal of water is a key factor in the successful reduction of catalysts



Metal Oxide Reduction



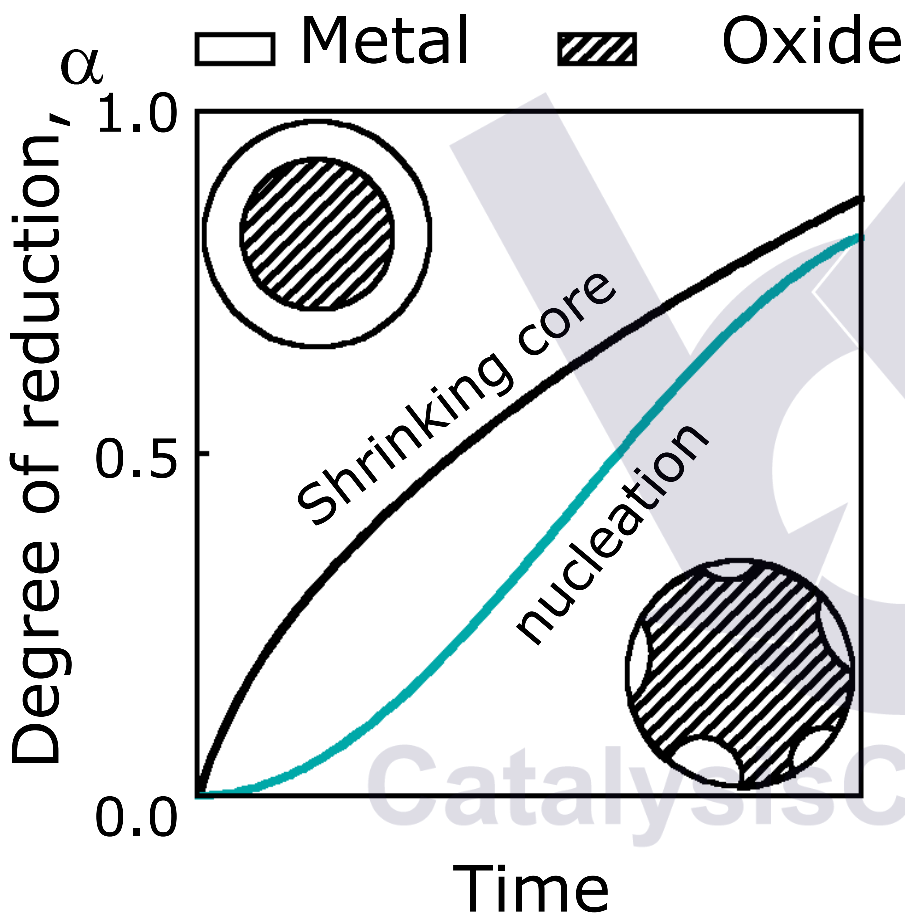
Nucleation: reduction by H_2

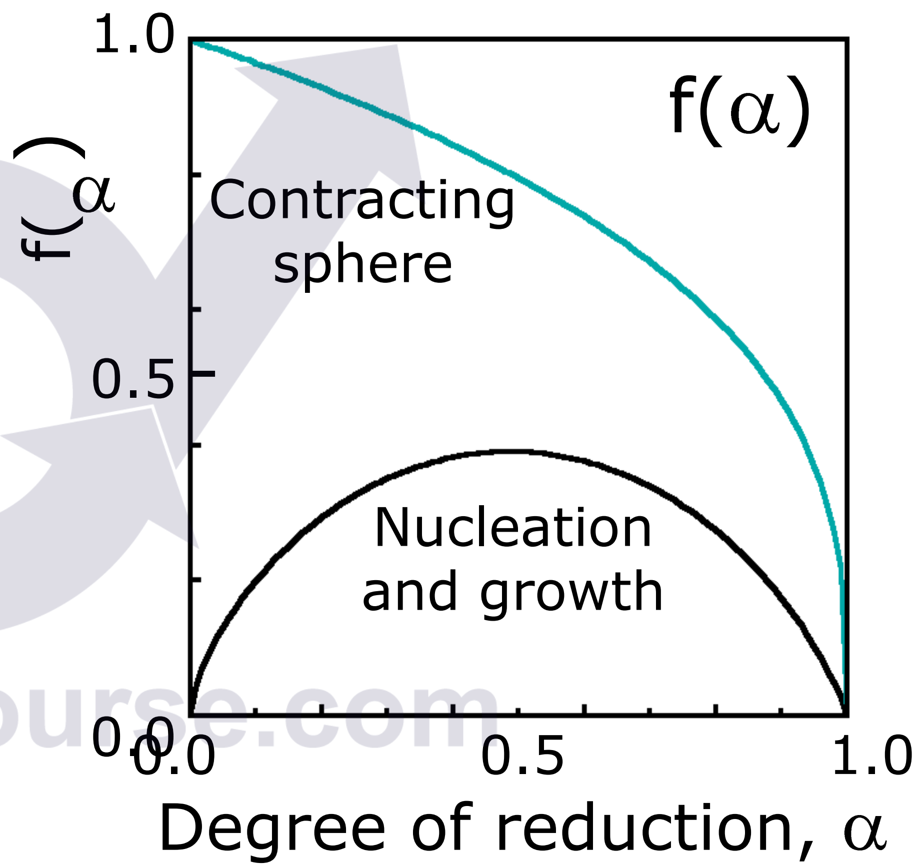
- slow for non-noble metals;
- fast(er) for noble metals

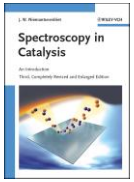
Growth: reduction by H

(fast)

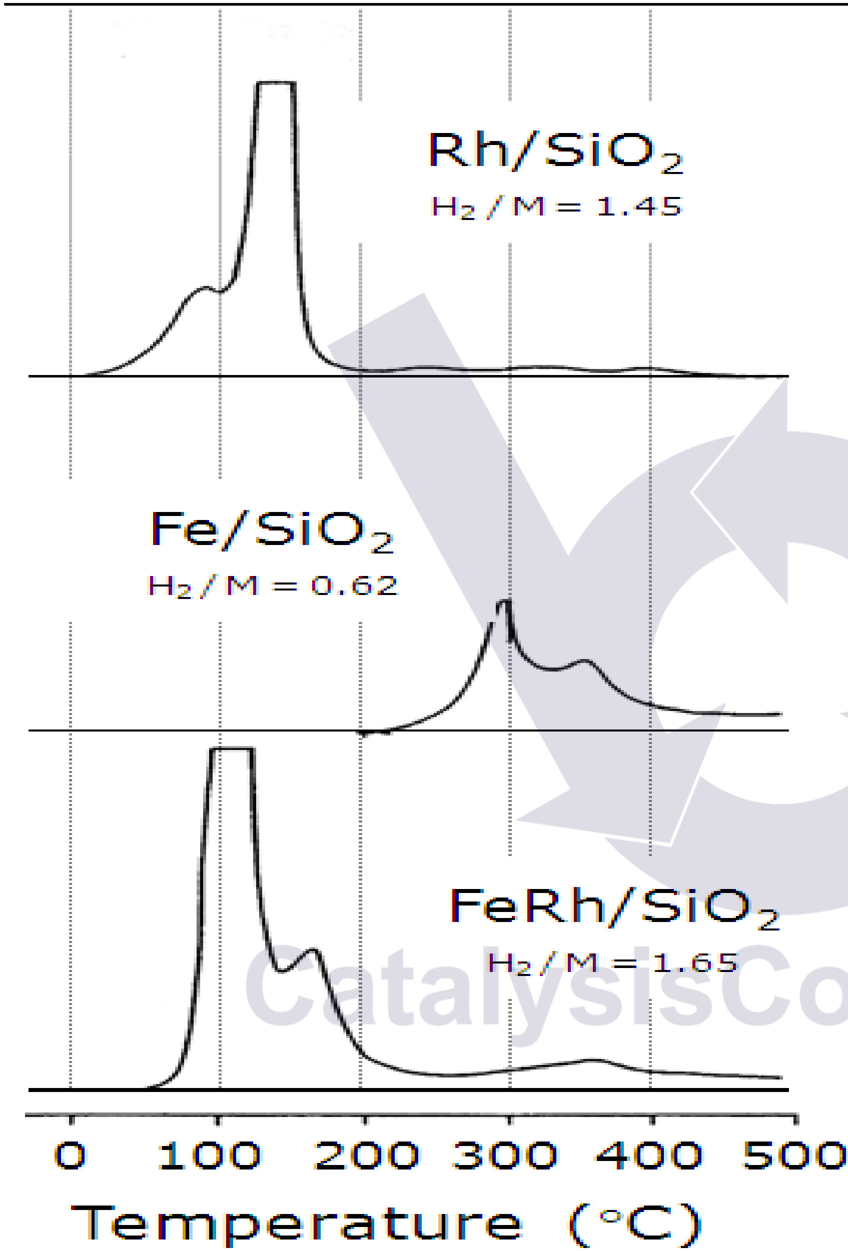
Metal Oxide Reduction







Example: TPR of supported catalysts



Full reduction:

$Rh_2O_3 + 3\ H_2 = 2\ Rh + 3\ H_2O$
$H_2/Rh = 1.5$

$Fe_2O_3 + 3\ H_2 = 2\ Fe + 3\ H_2O$
$H_2/Fe = 1.5$

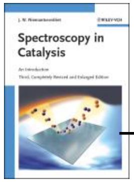
$Fe_3O_4 + 4\ H_2 = 3\ Fe + 4\ H_2O$
$H_2/Fe = 1.33$

$FeO + H_2 = Fe + H_2O$
$H_2/Fe = 1.0$

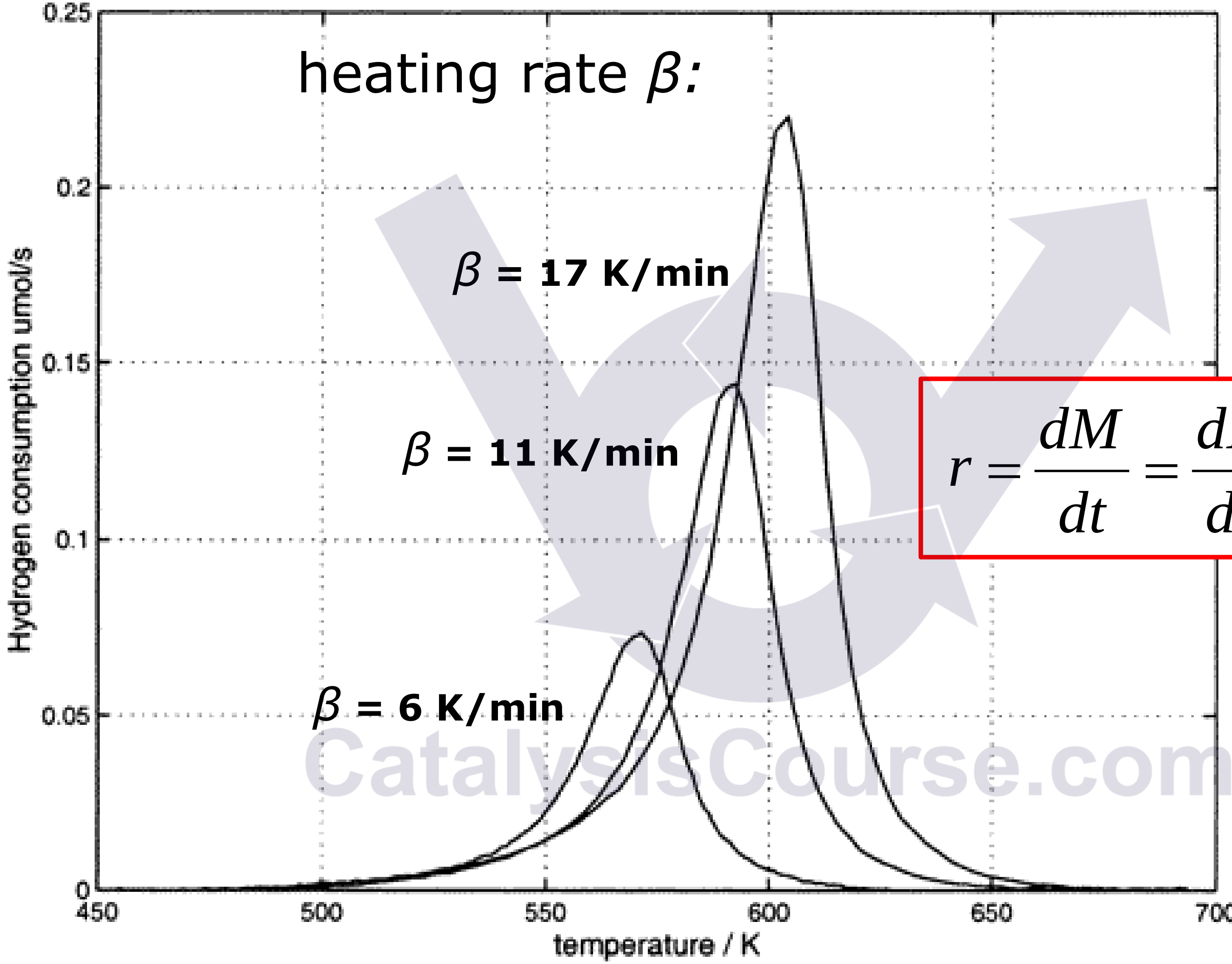
Reduction promotion:

- Noble metal Rh assists in the reduction of the less noble Fe
- Rh metal nucleates fast; this enables H_2 dissociation; H-atoms reduce the iron oxide

H.F.J. van 't Blik and J.W. Niemantsverdriet, Appl. Catal. 10 (1984) 155



TPR: Effect of Heating Rate - CrO_x / Al_2O_3



$$r = \frac{dM}{dt} = \frac{dM}{dT}\frac{dT}{dt} = \beta\frac{dM}{dT}$$

J.M. Kanervo and A.O.I. Krause, J. Phys. Chem. B 105 (2001) 9778

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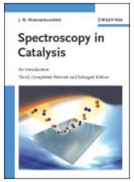
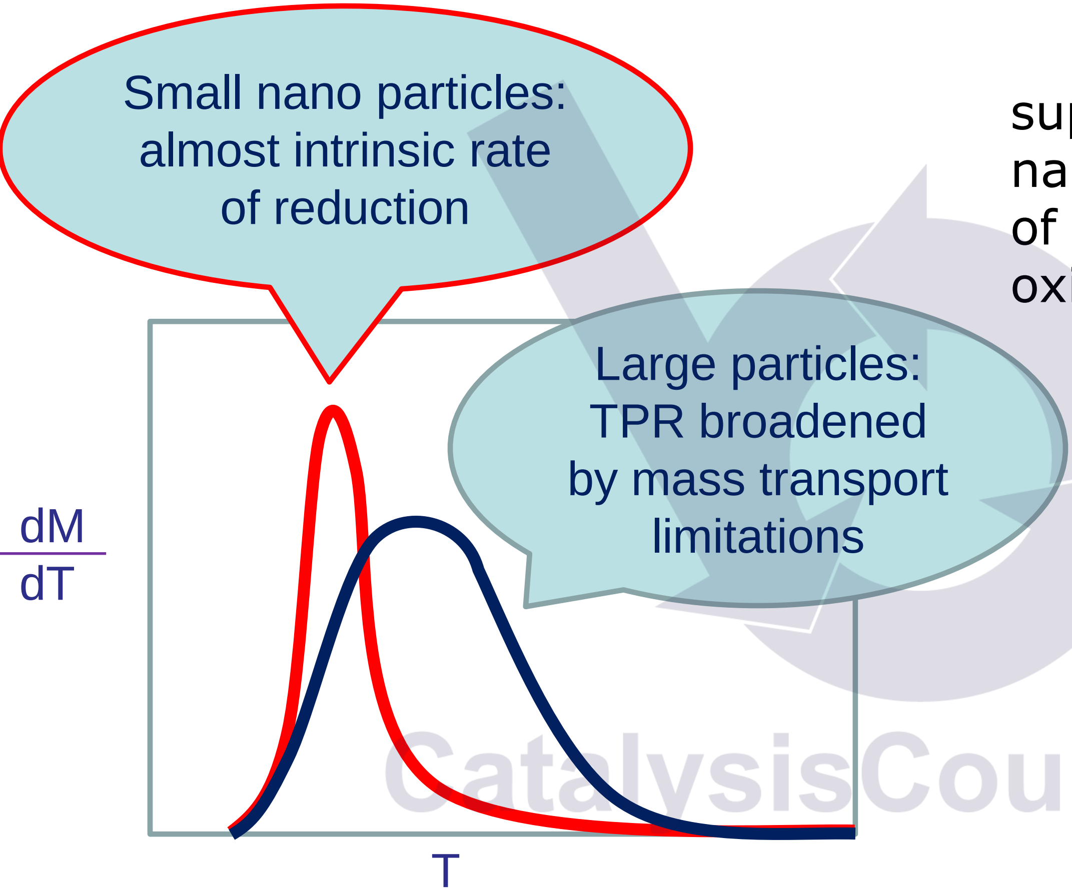


TPR: Effect of Particle Size



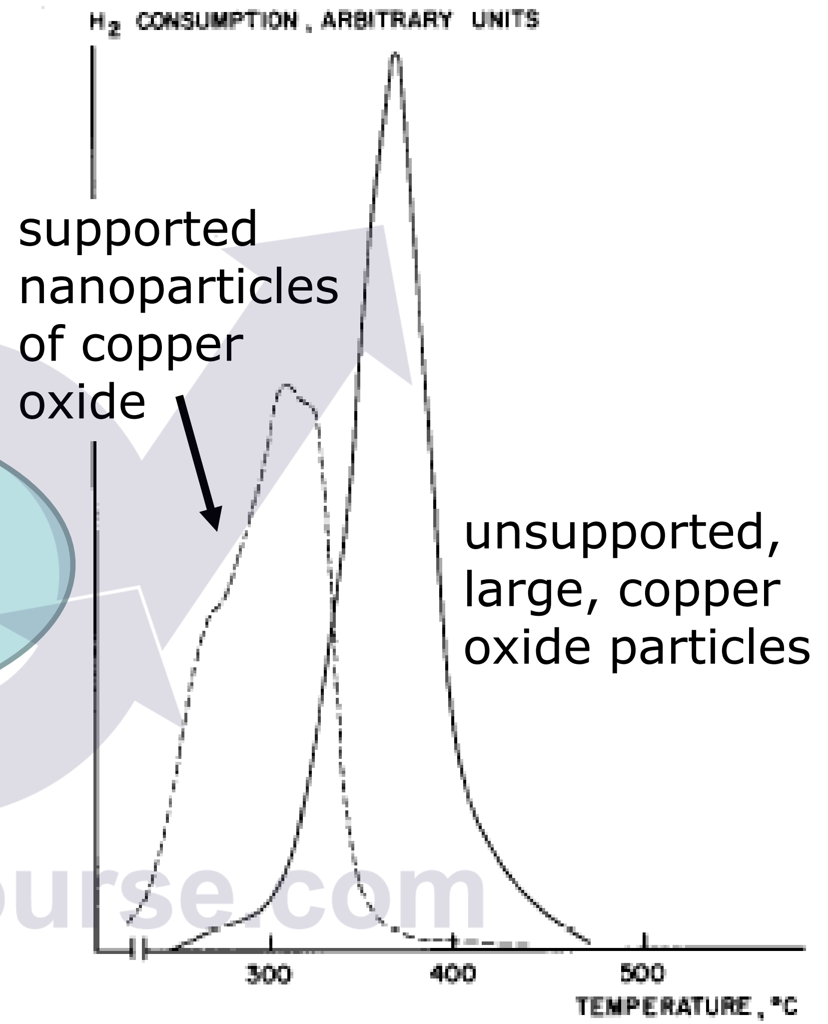
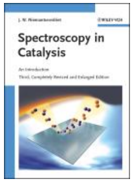
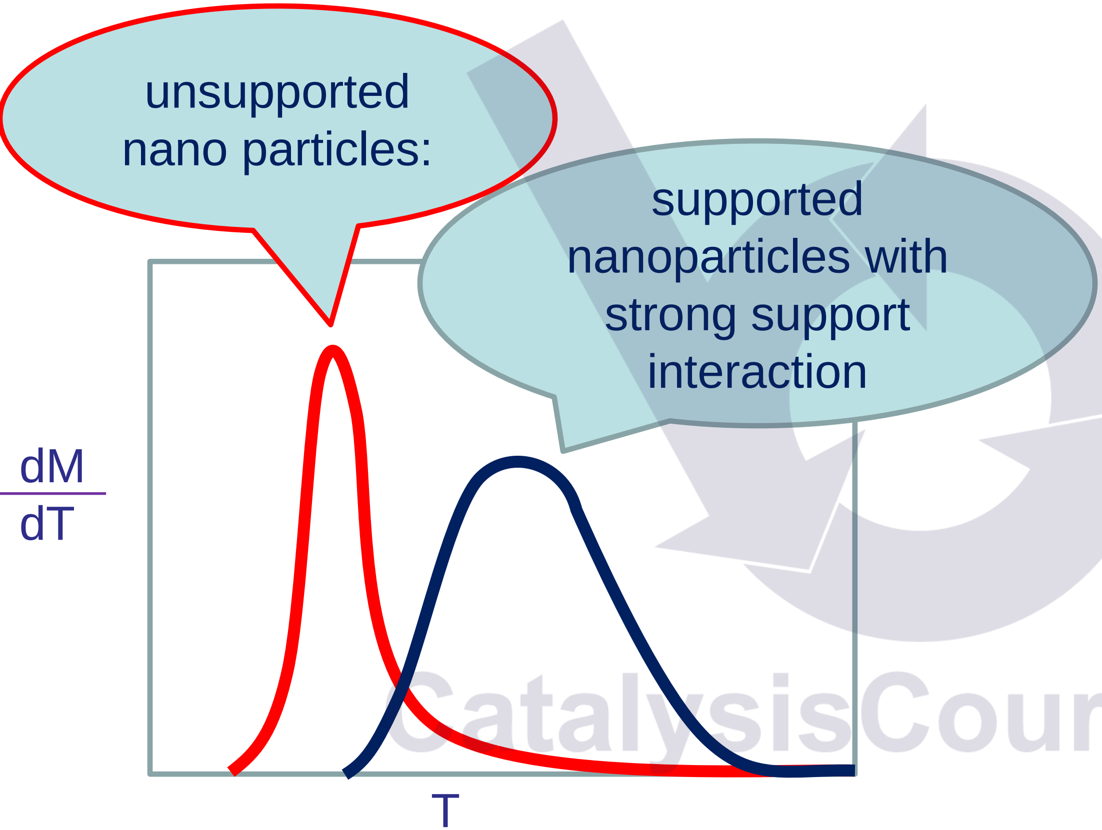


Fig. 3. Temperature-programmed reduction of unsupported and silica-supported copper oxide.

S.D. Robertson, B.D. McNicol, J.H. de Baas, S.C. Kloet, and J.W. Jenkins, J. Catal. 37 (1975) 424



TPR: Effect of Support Interaction



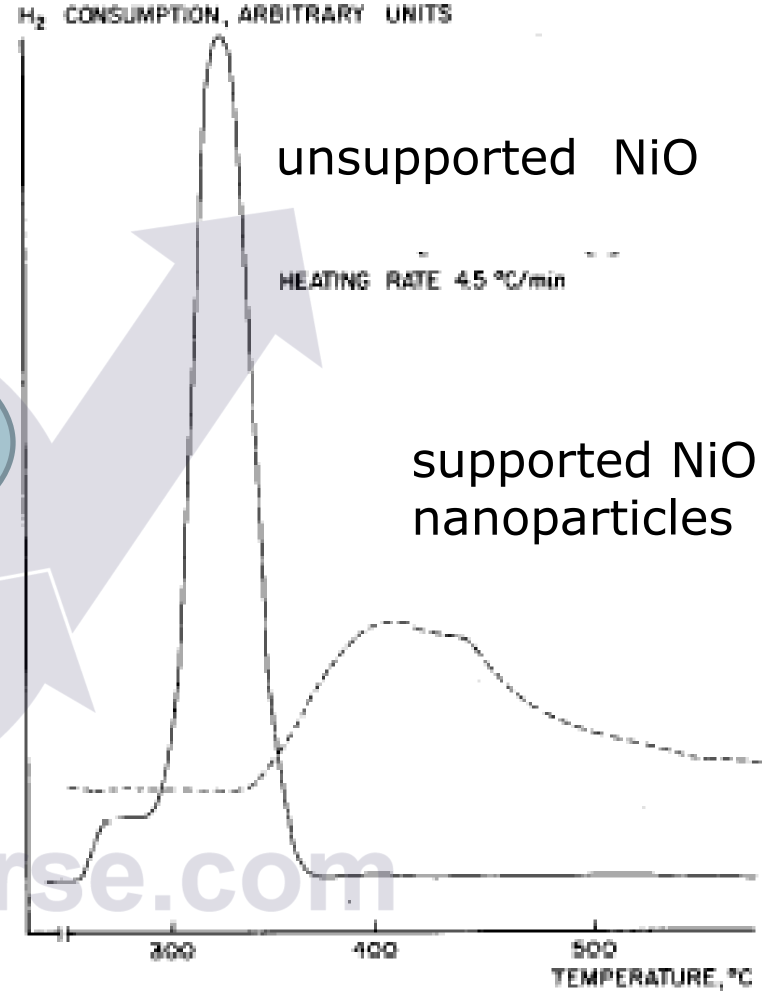
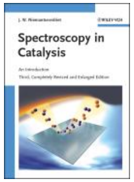


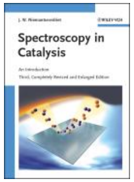
FIG. 2. Temperature-programmed reduction of unsupported and silica-supported nickel oxide.

S.D. Robertson, B.D. McNicol, J.H. de Baas, S.C. Kloet, and J.W. Jenkins, J. Catal. 37 (1975) 424

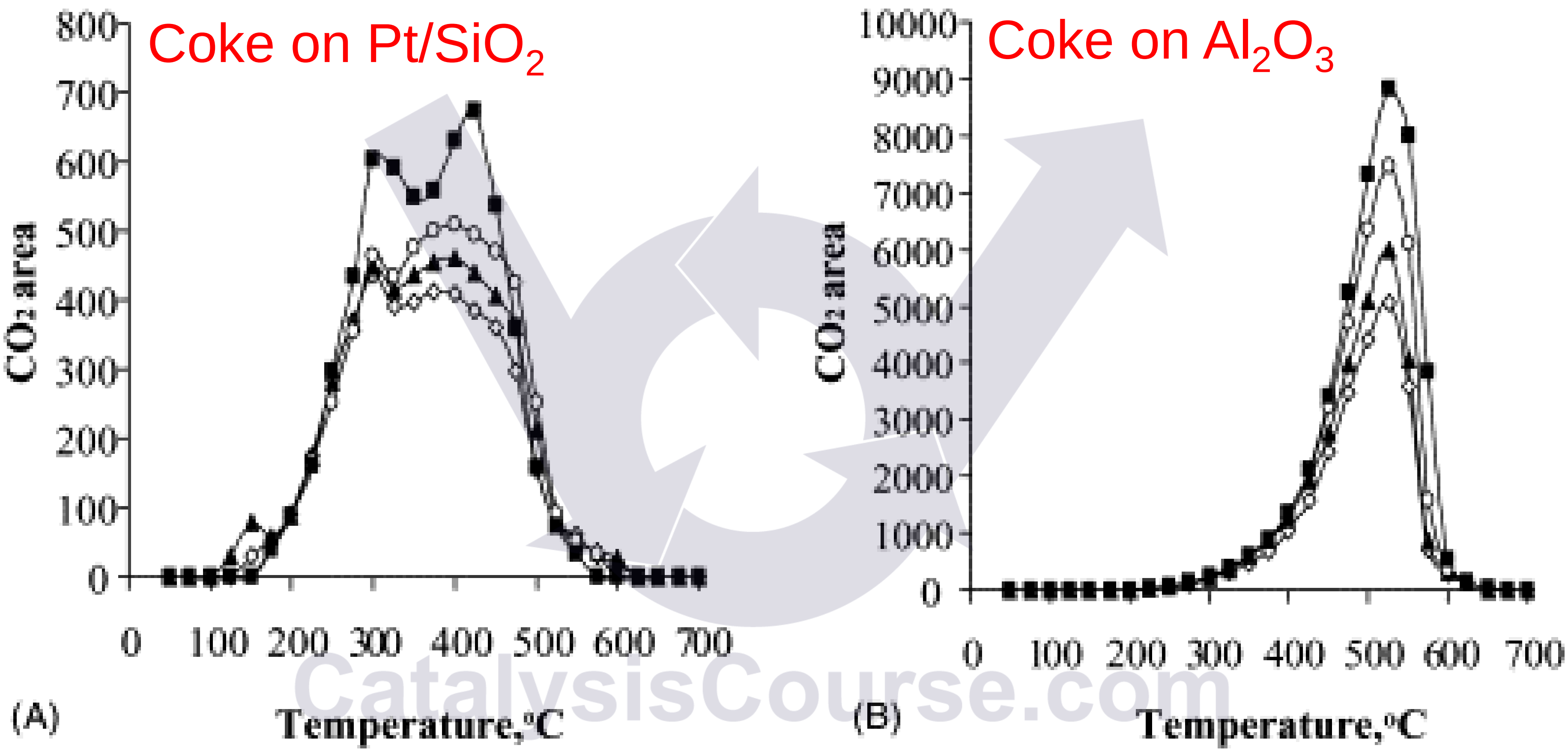


Temperature Programmed Techniques

TPR	**Reduction**
TPO	**Oxidation**
TPS	**Sulfidation**
TPD	**Desorption**
TPRS	**Reaction Spectroscopy**



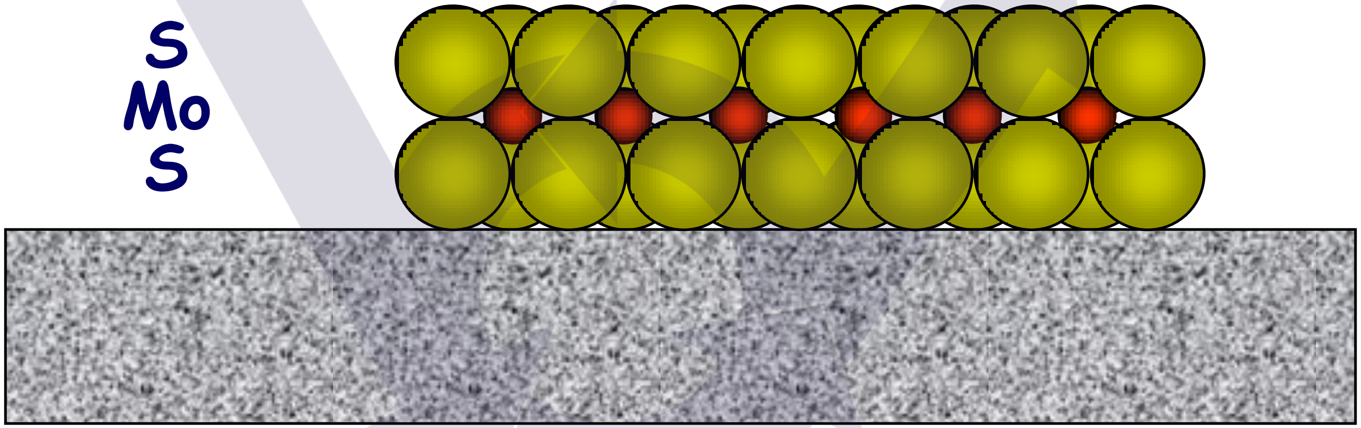
TPO of coke on catalysts



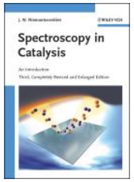
S. SRihiranpullop and P. Praserthdam, Catal. Today 93-95 (2004) 723

Active phase in hydrotreating catalysts:

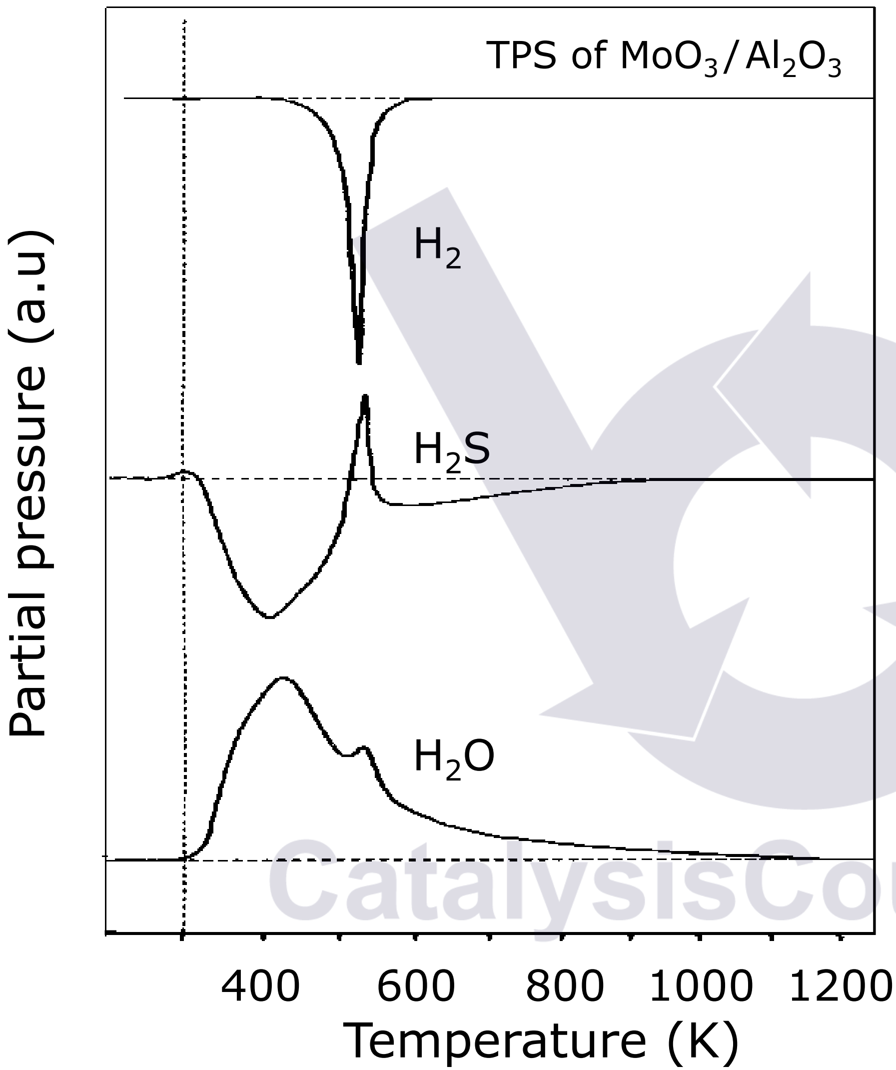
sulfides (e.g. MoS_2)



Catalysts are prepared by sulfiding oxides with H_2S / H_2 mixtures



Temperature Programmed Sulfidation



MoO_3

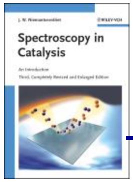
↓

$MoO_xS + MoS_3$

↓

MoS_2

P. Arnoldy, J.A.M. van den Heijkant, G.D. de Bok and J.A. Moulijn, J. Catal. 92 (1985) 35.



Temperature Programmed Techniques

TPR	**Reduction**
TPO	**Oxidation**
TPS	**Sulfidation**

information on

- **reaction temperature**
- **extent of reaction (degree of reduction)**
- **reaction mechanism**

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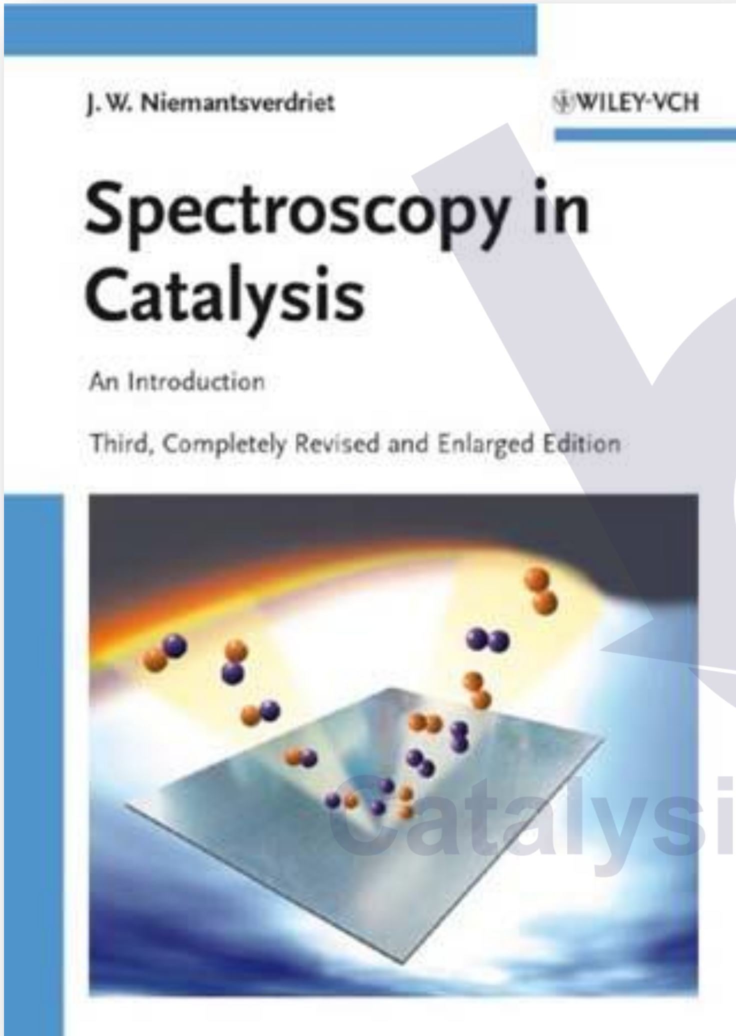

Read more about temperature-programmed techniques in

Chapter 2 of

Spectroscopy in Catalysis: An Introduction, Third Edition

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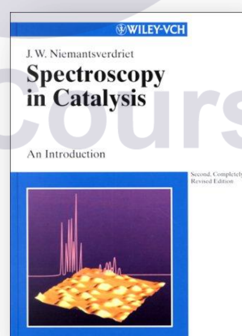

Version 2000

gives many examples and references to the literature

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