A practical model situation

- TPR of metal oxide by hydrogen diluted in nitrogen.
- Competitive adsorption of nitrogen (first order) and hydrogen (second order).
- Flow experiment (kinetic vs. thermodynamic control, re-adsorption).





Parameters of the first-order model

Parameter	Value	Dimension
S	1×10^6	cm^2/g
N *	1×10^{-9}	mol/cm ²
σ	9.8×10^8	cm ² /mol
Μ	28 ^a	g/mol
	2^{b}	g/mol
R	8.314	J/(K·mol)
F	10	$\mathrm{cm}^3/\mathrm{s}\cdot\mathrm{g}$)
β	0.1	K/s
Ea ^C	10.0×10^{3}	J/mol
Ac	1 ^a	_a
	1×10^{9b}	cm ² /mol ^D
e d	60.0×10^3	J/mol
Ad	1×10^{10} to 1×10^{13}	$s^{-1}a$
u	1×10^{19} to 1×10^{22}	$\mathrm{cm}^2/(\mathrm{s}\cdot\mathrm{mol})^\mathrm{b}$



model results: activation energies





Temperature-programmed methods









Reaction rate: second order

$$C_{(T)} = \frac{S + N^{*2} \Theta^2 A_d \exp^{(-E_d/RT)}}{F + S N^{*2} (1 - \Theta)^2 \sigma (RT/2\pi M)^{1/2} A_a \exp^{(E_d/RT)}}$$

$$\Theta/dT = -\frac{F}{S \beta N^*} C_{(T)}$$

Dissociative adsorption requires two sites per elementary step. Still simplistic, as no provison for surface re-arrangement of the adsorbates is being made: further terms are required, in particular for strongly sticking molecules or at low temperatures



d



Model: second order





Temperature-programmed methods



Model: second order





Temperature-programmed methods



Ag-O: functional distinction of oxygen 02 Ag(111) οα O_{γ} O_β sub-oxide oxidising basic oxidation epoxidation de-hydrogenation Local chemical bonding metal oxide ecides Tower ature programmed methods total oxidation AV. DIANCE CESELISCHAE

Oxidative Dehydrogenation of Methanol over Ag



Analytical data and temperatureprogrammed reaction experiments suggest several independent reaction channels and hence several active oxygen species.



L. Lefferts, J.G. van Ommen, J. H.R. Ross, Trans. Faraday Soc., 84, (1988), 1491

Temperature-programmed methods

Oxidative Dehydrogenation of Methanol over Ag



Surface science model experiments identify one chemically active atomic oxygen species

Assigning , however several chemical functions to the

same specis (acie base vs. oxidative)

adix, J.T. Reproperiate Series in Syram Repetion and Hod 894, p.9



rds in OCM





Selective and Total Oxidation of MeOH

There are clearly two reaction pathways for MeOH oxidation with differing selectivities

Electrolytic silver

pre-dosing with 100 mbar oxygen at 873 K for 5 min

hodsin MeOH at 10⁻⁵ mbar



Ag as Storage Medium for Active Oxygen



In analogy to "lattice oxygen" Ag can store selectively acting atomic oxygen.

Under the conditions of a pulse experiment at ambient pressure formic acid is a consecutive

product.



Ag-O: speciation by TDS



TDS allows to isolate 3 diffrent atomic oxygen species

Catalyst conversion coincides not with the ,,surface atomic" oxygen

species

AC

Temperature-programmed methods

MAX-PLANCK-GESELLSCHAFT

Ag-O: solid state transformation in TDS multiple



multiple experimental series are required to obtain characteristic desorption traces

high-pressure dosing and cyclisation essential,

FHI The changes in ordinate scale!

little effect in static experiments



The non-equilibrium nature



The identification of bulk dissolved and surfaceembedded oxygen depends critically on the conditions of TDS (2.5 K/s)

 $\stackrel{\cong}{\vdash}$ Electrolytic silver

pre-dosing with 100 mbar oxygen at 873 K for 5 min





Facetting

in oxygen

FHI

Ag-O: mode of action: MeOH



Surface abundance of alpha oxygen (green) is detrimental for selectivity

> Alpha oxygen is required to form other atomic oxygen species:

Site separaton



Mode of Action in EO Synthesis



The presence of dehydrogenating oxygen (purple) next to electrophilic oxygen is detrimental for the selectivity.





TPR

- Reduction of a metal oxide is a frequent process to generate metal catalysts
- In oxidation cataylsis it occurs as deactivation process and is undesired.
- As gas solid interaction it is very dependent on kinetic details.





TPR: A Chemical Process

$$-\frac{d[MO_n]}{dt} = k_{red} [H_2]^p f([MO_n])$$

in which

k_{red}

- $[MO_n]$ is the concentration of metal oxide
- [H₂] is the concentration of hydrogen gas
 - is the rate constant of the reduction reaction
 - is the order of the reaction in hydrogen gas
 - is the function which describes the dependence of the rate of reduction on the concentration of metal oxide is the time.

A model function is required





(2-4)

TPR: The observation

$$\frac{d\alpha}{dT} = \frac{\nu}{\beta} e^{-\frac{E_{red}}{RT}} f(1-\alpha)$$







TPR: Simple model functions







TPR: Thermodynamics

- Many reductions are only weakly exothermic.
- The virtual partial pressure plays an important role in controlling the extent of reaction.
- Great care must be taken in experimental analysis.
- Often water is added to feed to control the reduction extent.





TPR: Energetics

• The energetics is controlled by the chemical potential of the reductant:

 $\Delta G = n RT ln [(pH_2O/pH_2)/pH_2O/pH_2)eq]$







Metal	Oxide	$(p(H_2O)/p(H_2))_{eq}$
Ti	TiO ₂	4·10 ⁻¹⁶
	TiO	2.10-19
V	V_2O_5	6.10-4
	VO	$2 \cdot 10^{-11}$
Cr	Cr ₂ O ₃	3.10-9
Mn	MnO ₂	10
	MnO	$2 \cdot 10^{-10}$
Fe	Fe ₂ O ₃	0.7
deserve particular de la compañía d	FeO	0.1
Со	CoO	50
Ni	NiO	500
Cu	CuO	$2 \cdot 10^{8}$
	Cu ₂ O	2.10^{6}
Μο	MoO	40
	MoO ₂	0.02
Ru	RuO ₂	10 ¹²
Rh	RhO	10 ¹³
Pd	PdO	10 ¹⁴
Ag	Ag ₂ O	3·10 ¹⁷
Ir	IrO	1013



Temperature-programmed methods



TPR: An example



Bulk iron oxide particles in a TPR experiment: wet and dry relate to post-reaction drying of the same hydrogen stream





TPR: phase diagram and water



Water changes the reduction temperature drastically





TPR: Kinetics and Water



wet: 2% water in H₂

Wimmers et al: J. Phys. Chem., 90, (1986), 1331



