Catalytic Partial Oxidation
of low molecular-mass hydrocarbons

$$CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow CO_x$$
$$C_3H_8 \rightarrow C_3H_6 \rightarrow CO_x$$

M. Baerns

Lecture Series on Catalysis at FHI 2007/2008
Modern Methods in Heterogeneous Catalysis Research

Catalysis and Catalyst Properties

Reaction mechanisms and kinetic schemes

Effect of properties of solid materials on their catalytic performance

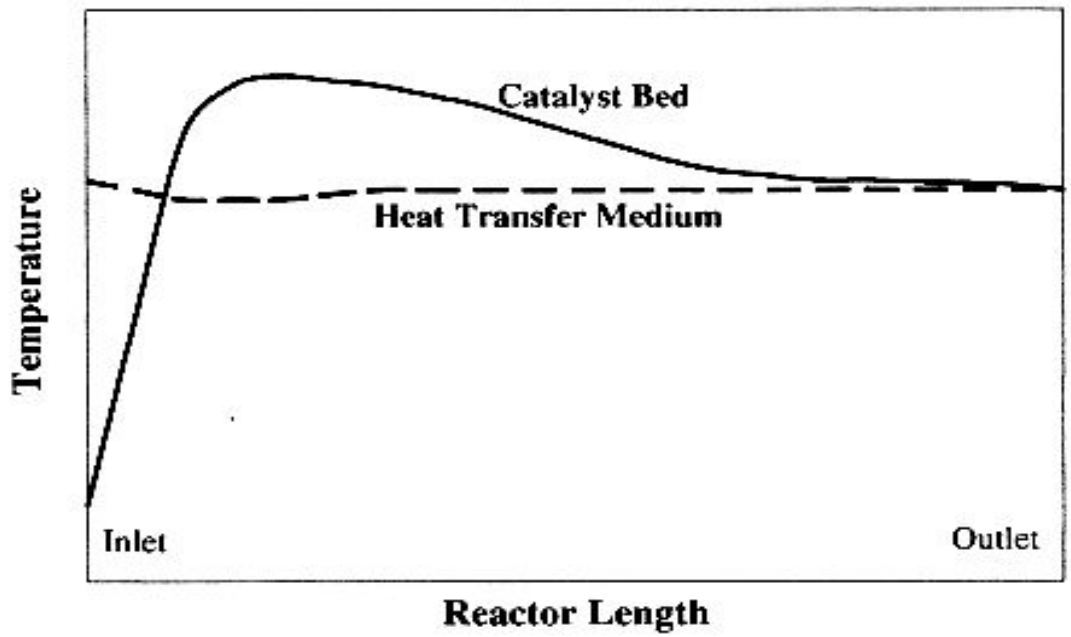
Subjects to be considered

- Interactions of gas-phase reactants with the catalyst surface, i.e., transformations of reactants on the catalyst surface
- Solid state transformations in catalyst preparation and operation
- Solid state properties

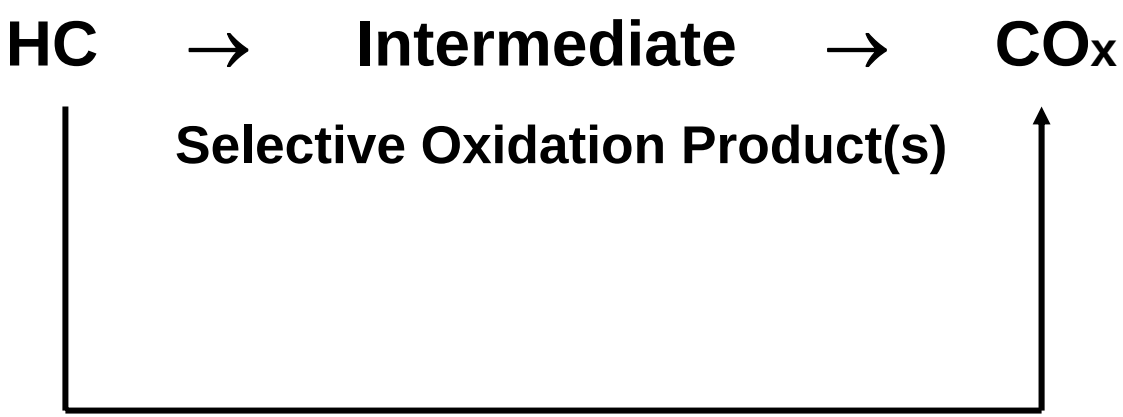
Reaction steps and kinetic schemes

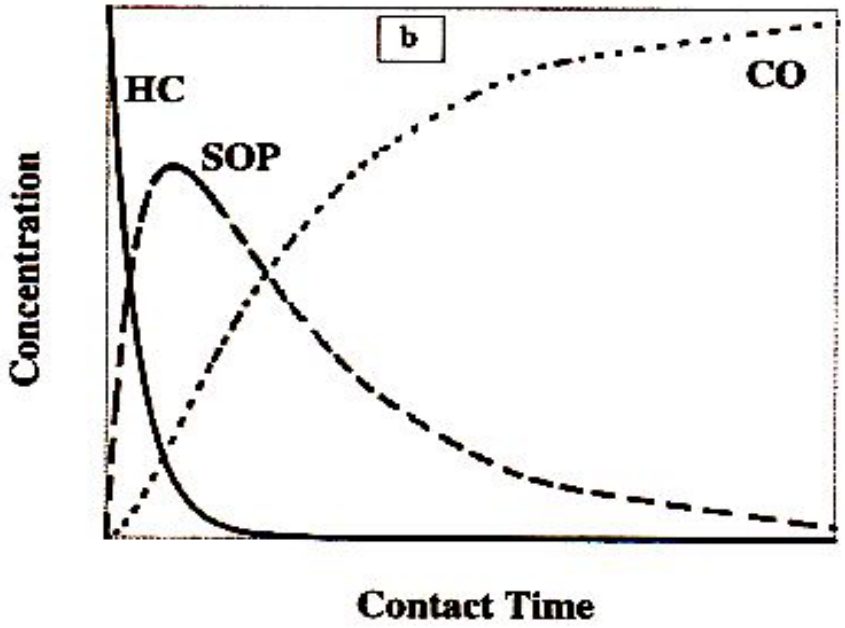
- Single and multiple surface reaction steps (with and without intermediate desorption steps)
- Parallel and consecutive reaction steps originating from one molecule influencing the selectivity of the desired product in such complex reaction networks as experienced in almost all hydrocarbon oxidation reactions.
- Quantitative description of reaction schemes by rate equations of the various reaction steps and correlating the rate constants with catalyst properties

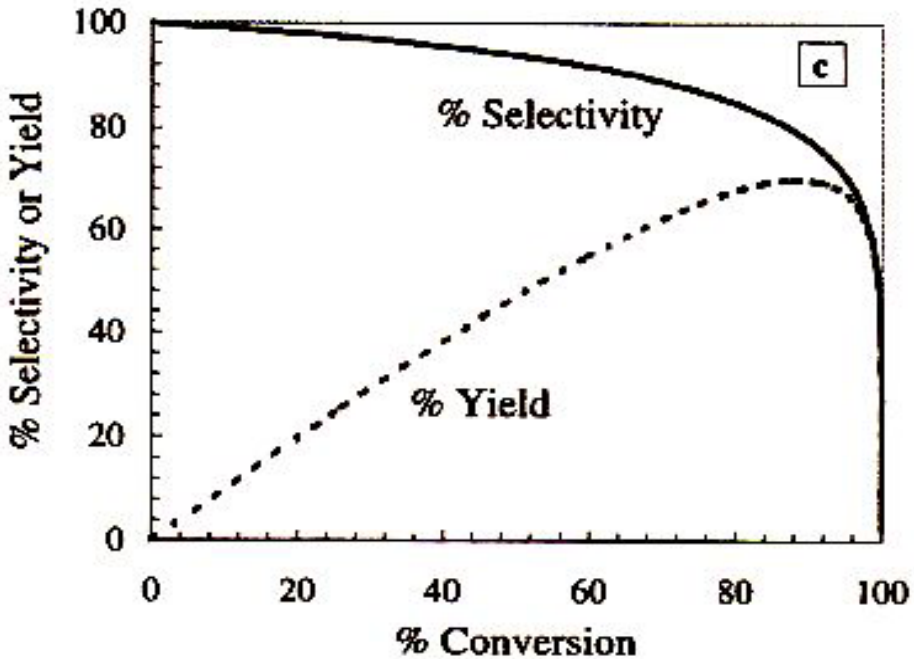
Temperature profile in and around a tubular continuous-flow catalytic reactor



Reaction Network in Selective Oxidation







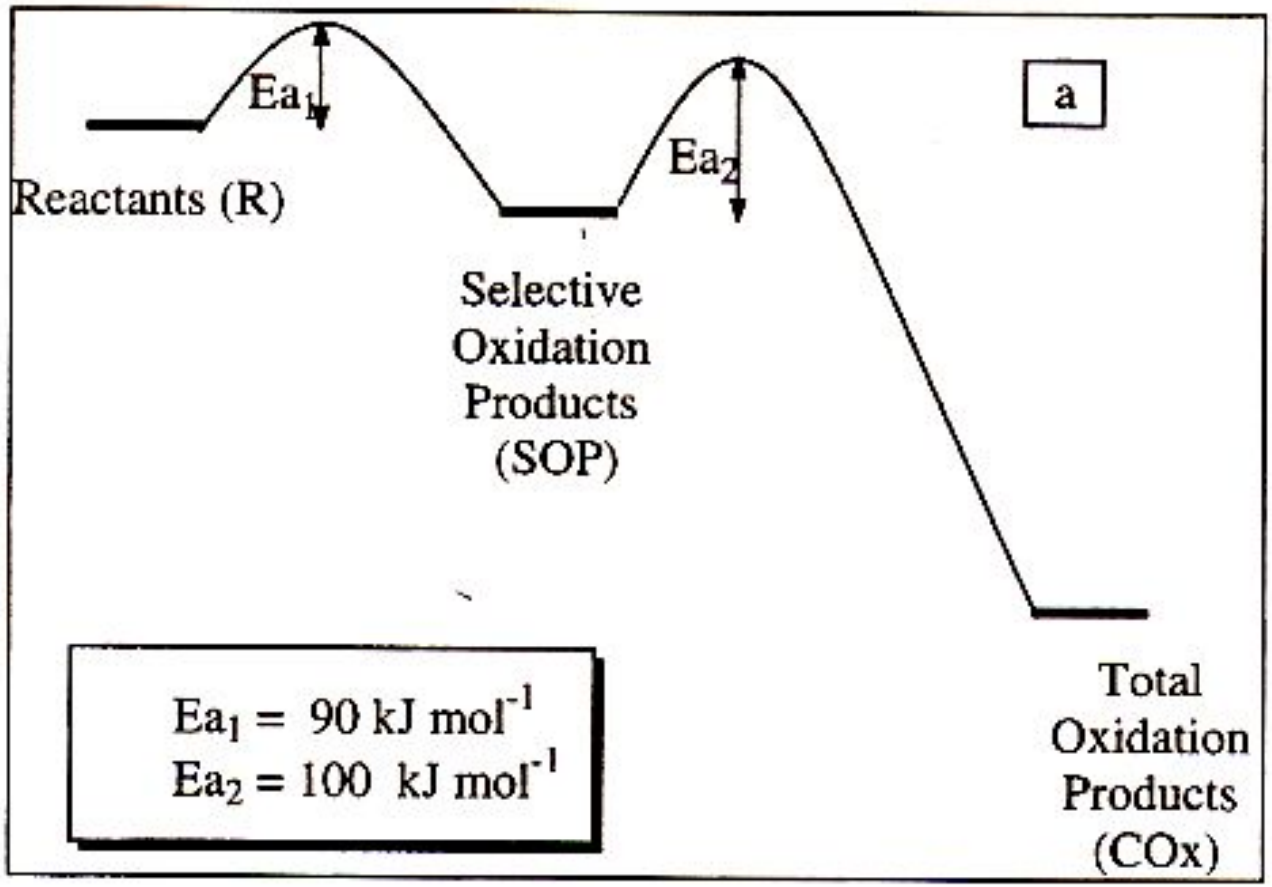
Parallel and consecutive reactions

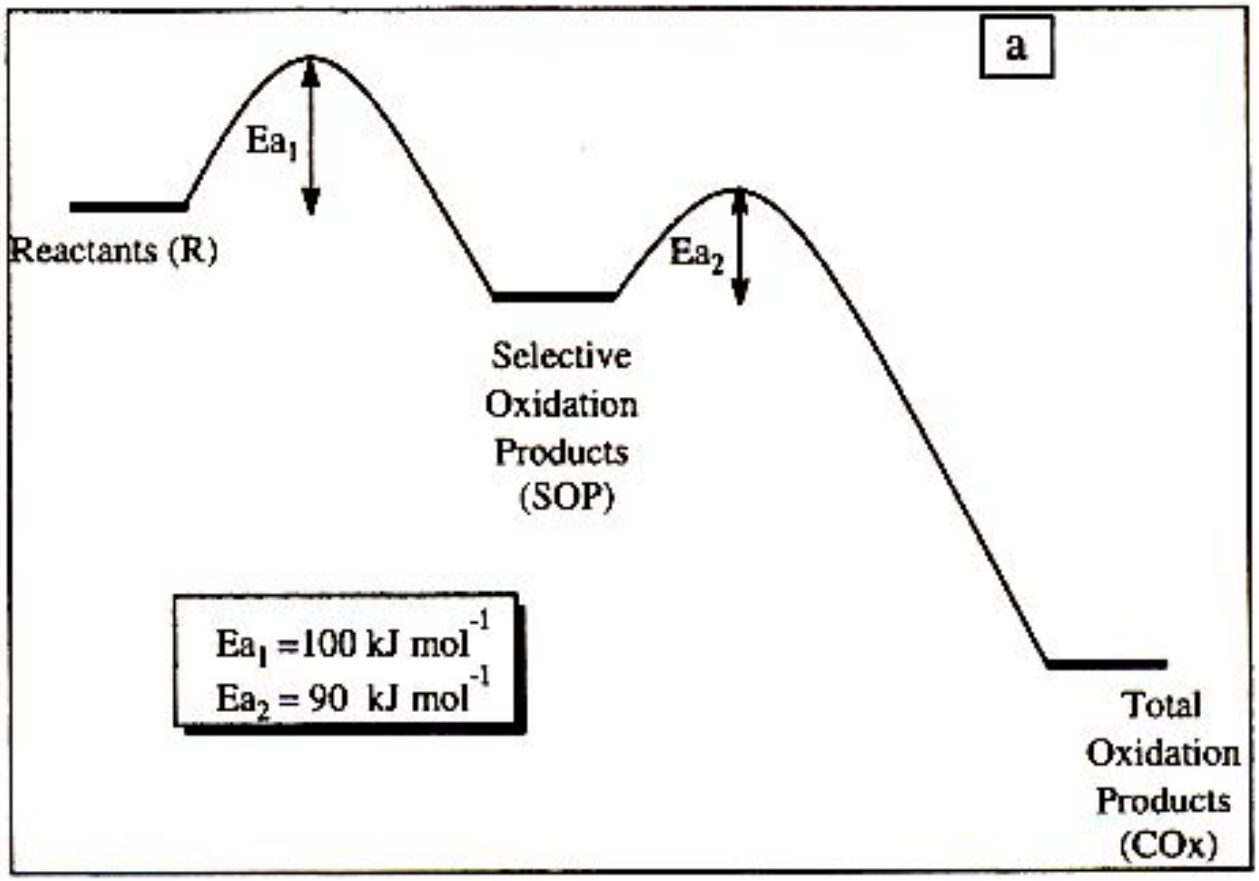
$C = f(\tau)$; $S = f(X)$

$S_P = n_P / (n_{k,0} - n_k)$; ($\nu$!!!)

$X_k = (n_{k,0} - n_k) / n_{k,0}$

$Y_P = S_P \cdot X_k$


Ea1
Ea2
a
Reactants (R)
Selective
Oxidation
Products
(SOP)
Ea1 = 90 kJ mol-1
Ea2 = 100 kJ mol-1
Total
Oxidation
Products
(COx)


a
Ea1
Reactants (R)
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(SOP)
Ea1 =100 kJ mol-1
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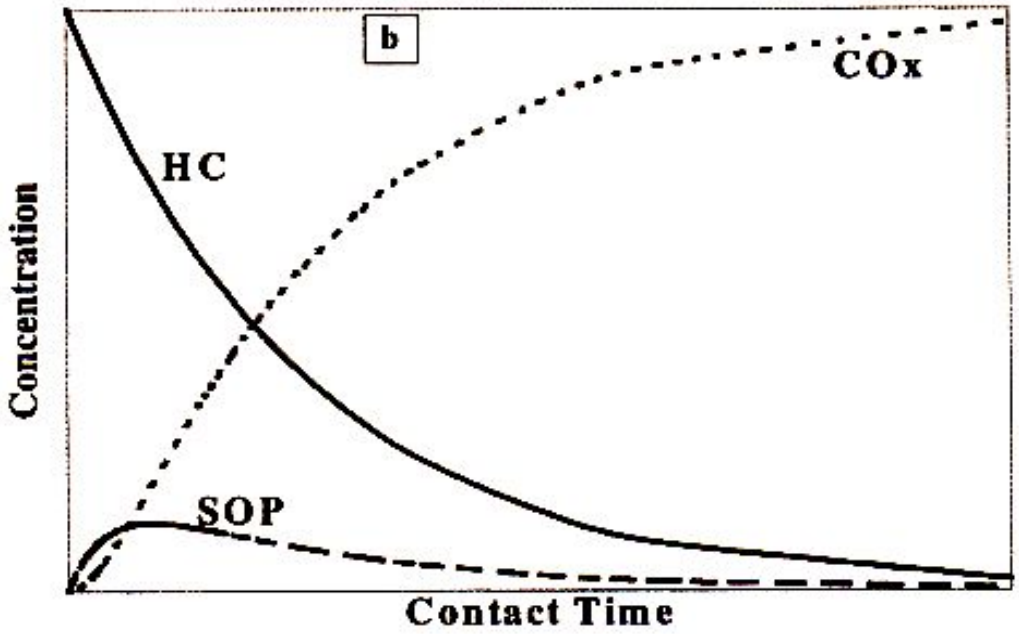

Parallel and consecutive reactions

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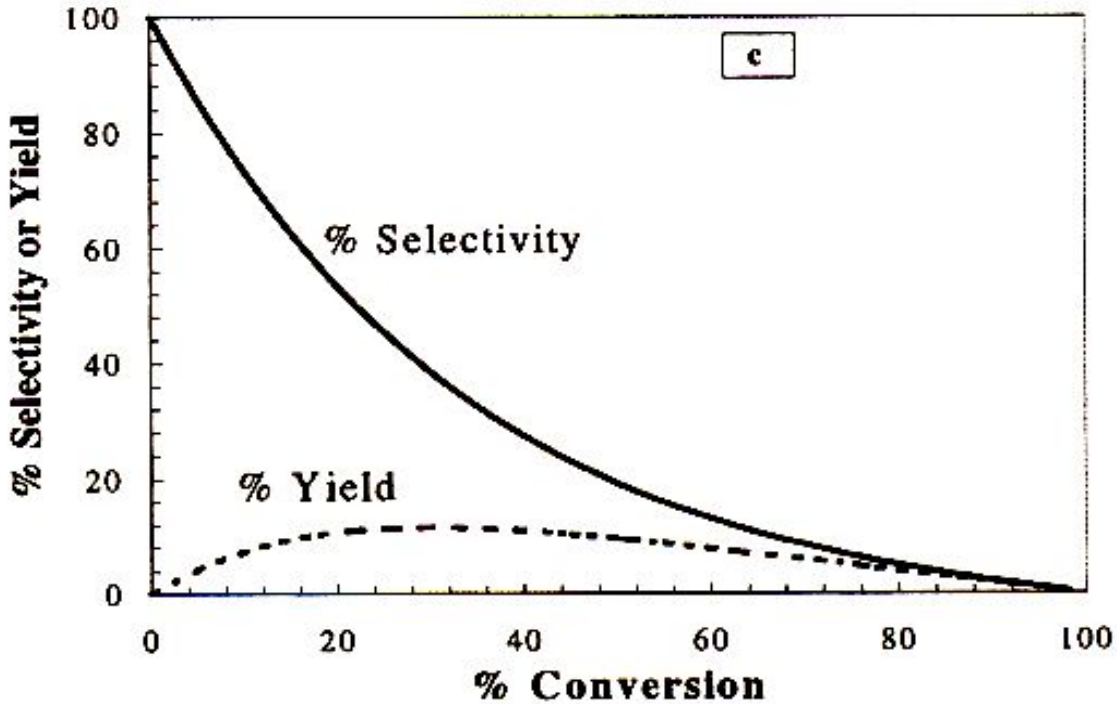
$Y_P = S_P \cdot X_k$



Elucidation of reaction mechanisms

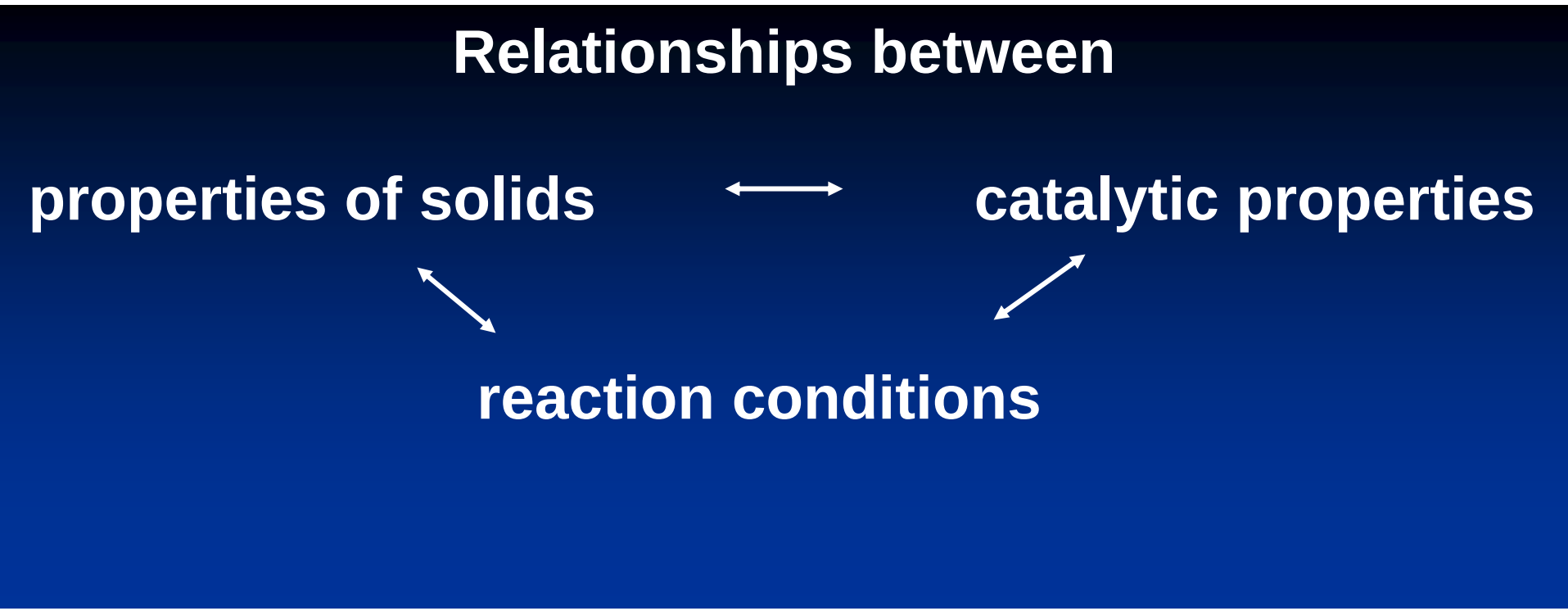
- solid state transformation in catalyst preparation and operation:
  e.g. amorphicity, crystallinity, phase transformations, ...
- solid state properties:
  e.g. bulk and surface structure & composition, basicity/acidity, el. conductivity, redox, ...
- gas-phase reactants:
  kinetic scheme
- interactions between gas-phase reactants and catalyst surface, i.e. transformation of reactants:
  e.g. ad- & desorption, bond breaking and forming, atom insertion & abstraction, ...

Selected Experimental Methods of Solids Characterization

XRD	LIF
XPS	FT-IR
SEM/EDX	FT-Laser-Raman
HREM	UV-vis
S(BET)	DRIFTS
(EELS)	ESR
(EXAFS)	DSC, DTA, DTG
(NEXAFS)	TPR, TPD, TPO, TPRS

R. Schlögl: In-situ Characterization of Pratical Heterogeneous Catalysts, in Ref. 2

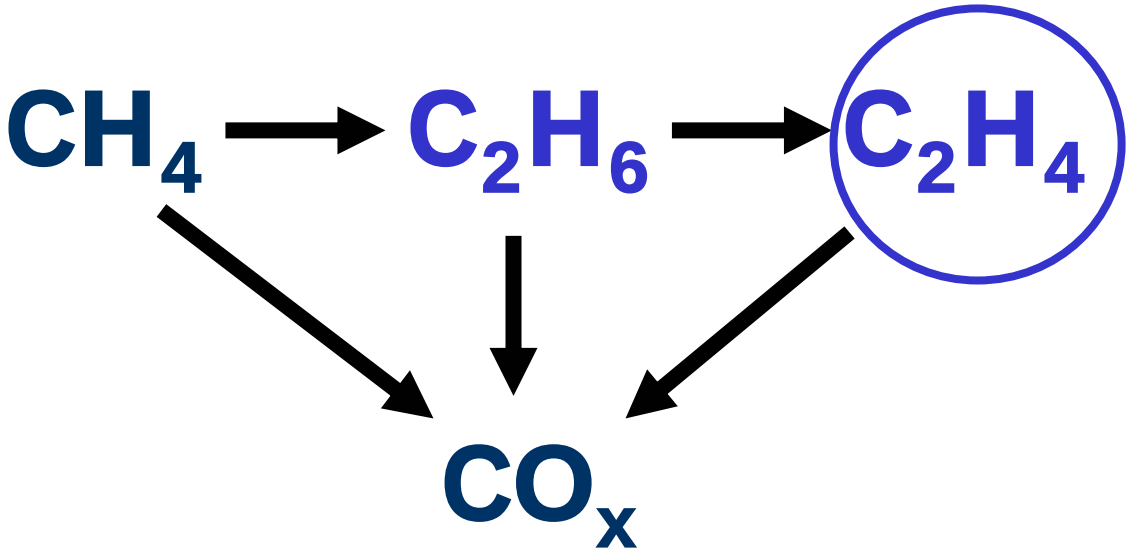
Interplay between surface and bulk properties of oxide catalysts for the selective oxidation



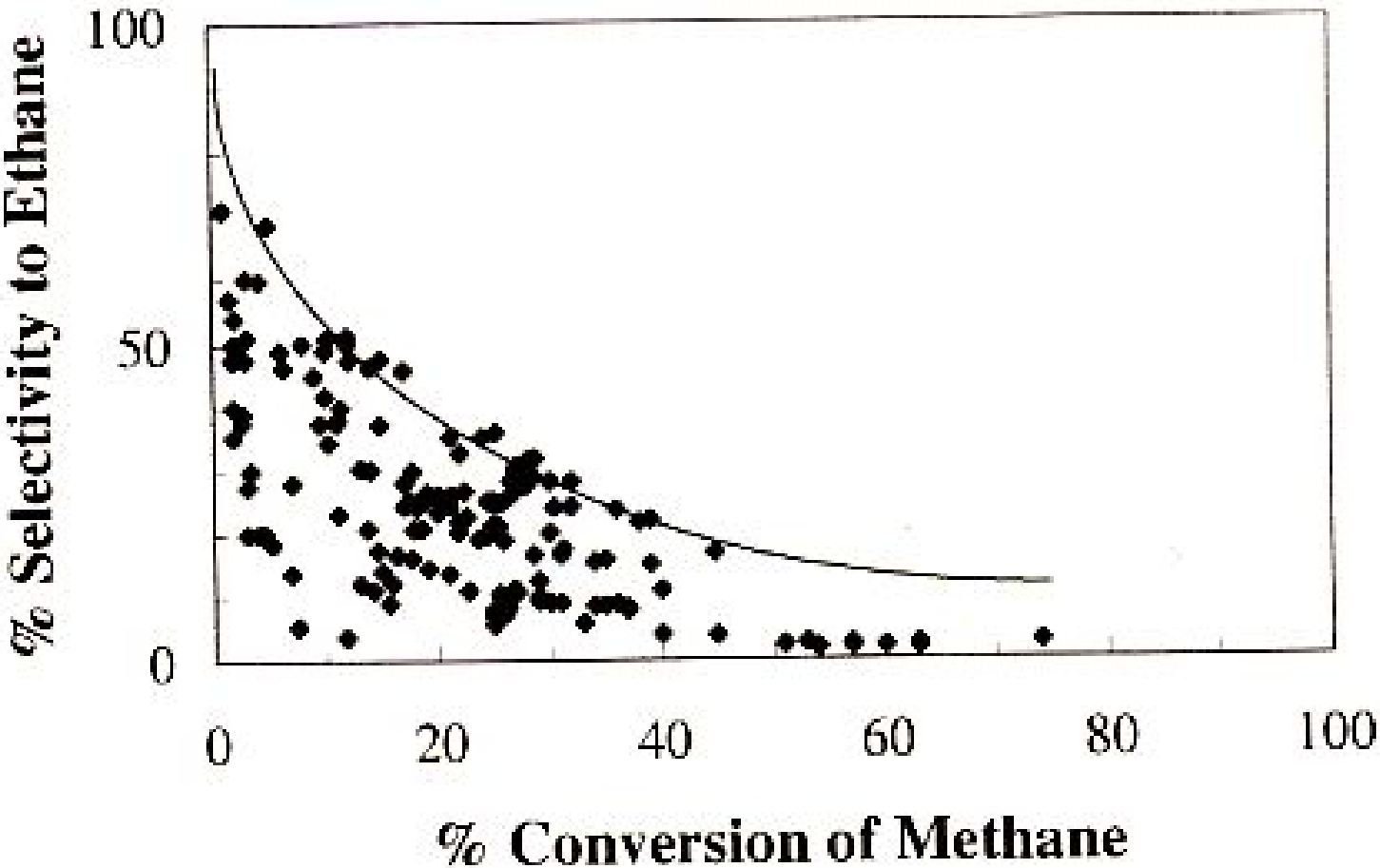
Part I

OCM

Oxidative coupling of methane
-Reaction scheme –

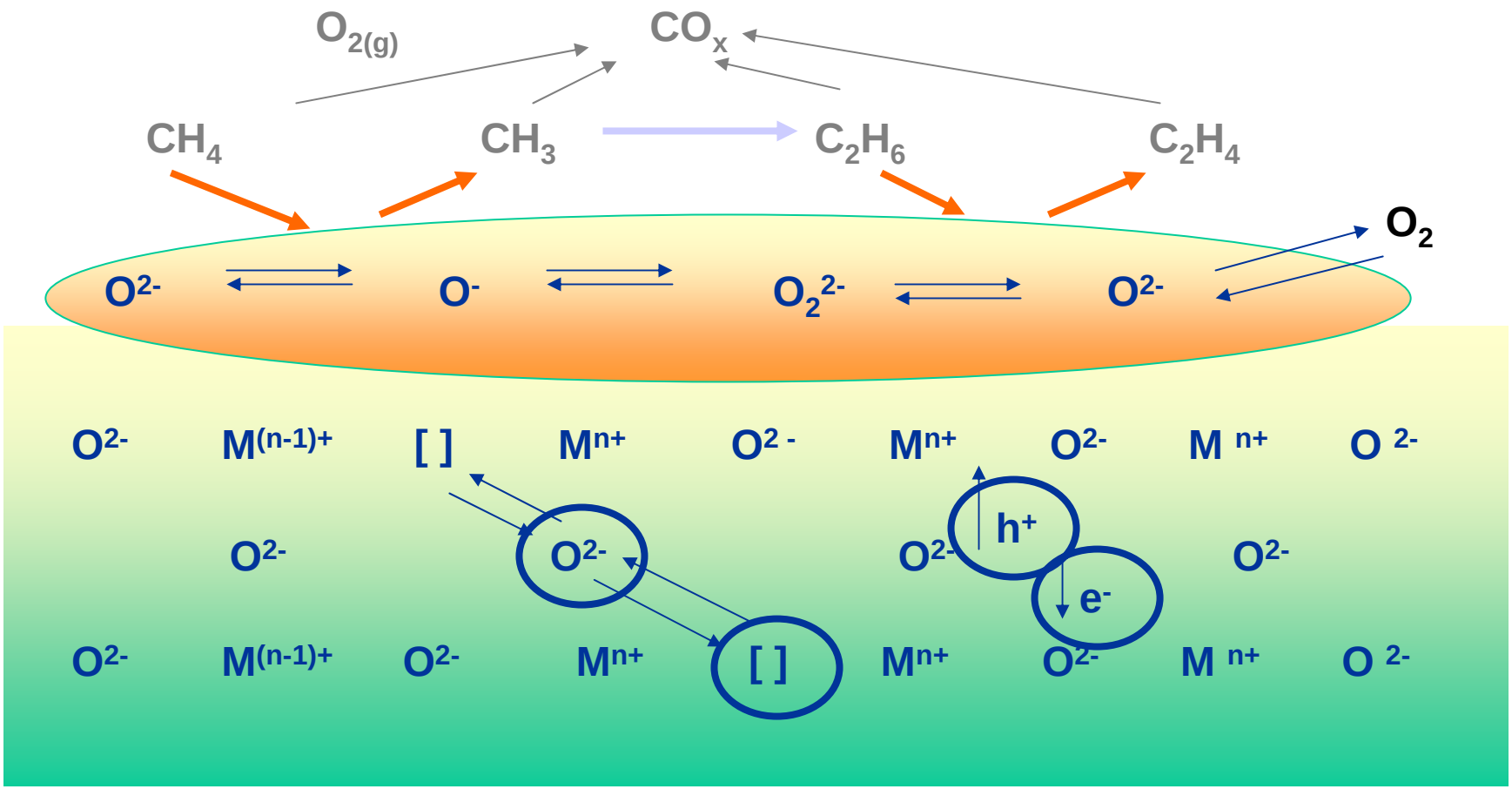


Typical pattern of dependence of selectivity on degree of conversion in the OCM rection



$CH_4 + O_2 \longrightarrow C_2H_6, C_2H_4$

over oxide-catalysts

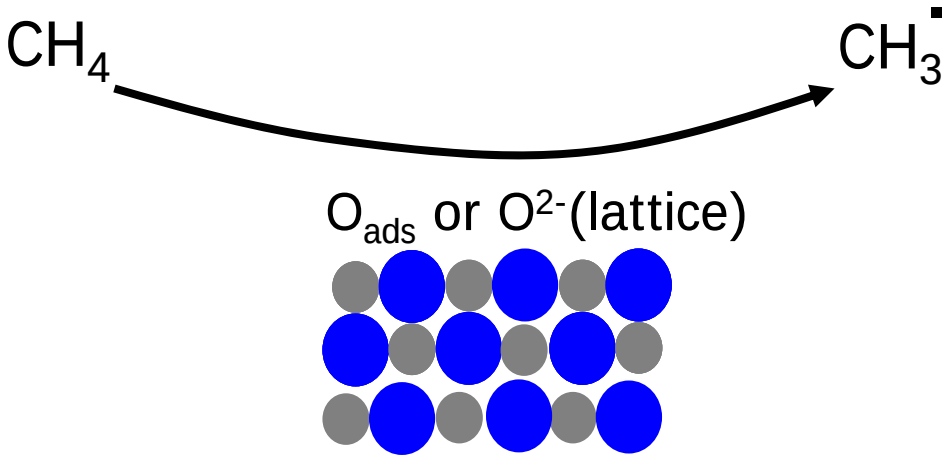


D. Wolf; Ruhr-Universität Bochum 1999,
DEGUSSA / EVONIK

Oxidative coupling of methane heterogeneous-homogeneous mechanism

Activation of CH_4

Heterogeneous process



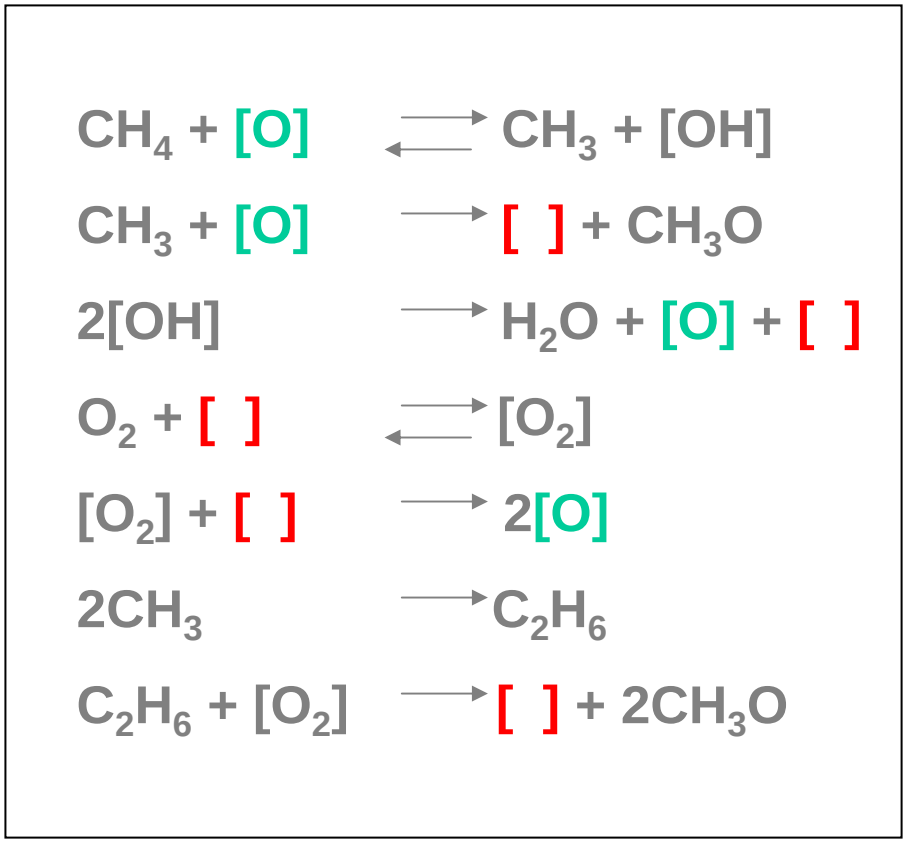
C_2H_6 formation

Homogenous process

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6$$

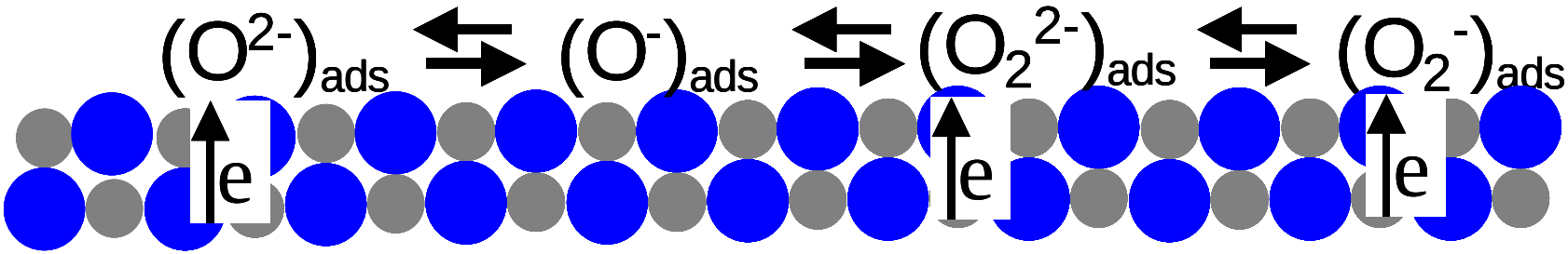
O.V. Buyevskaya et al., J.Catal. 146 (1994) 346
J. Lunsford et al., J.Catal. 147 (1994) 301

Reaction Scheme
(basis of kinetic analysis)

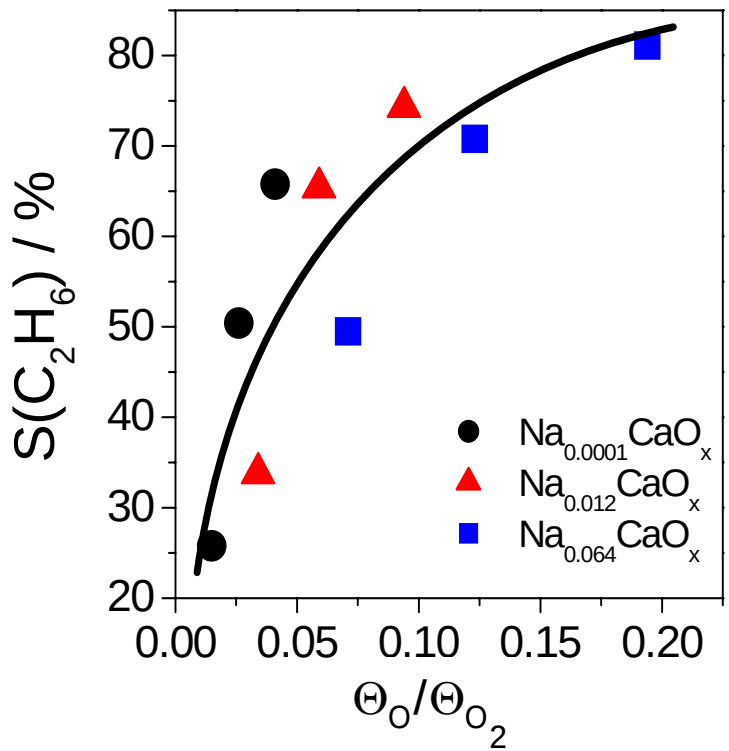


D. Wolf; Ruhr-Universität Bochum, 1999,
DEGUSSA / EVONIK

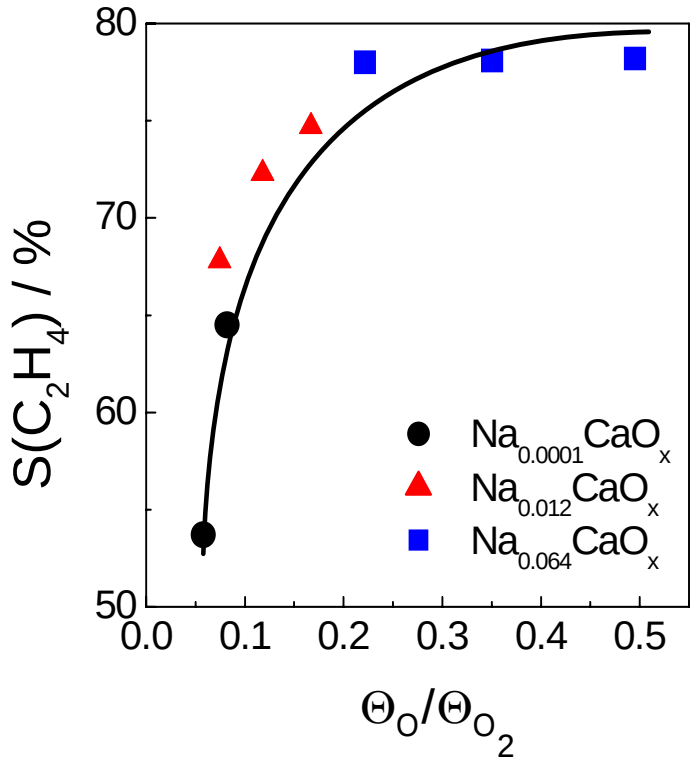
Electronic properties for O_2 activation



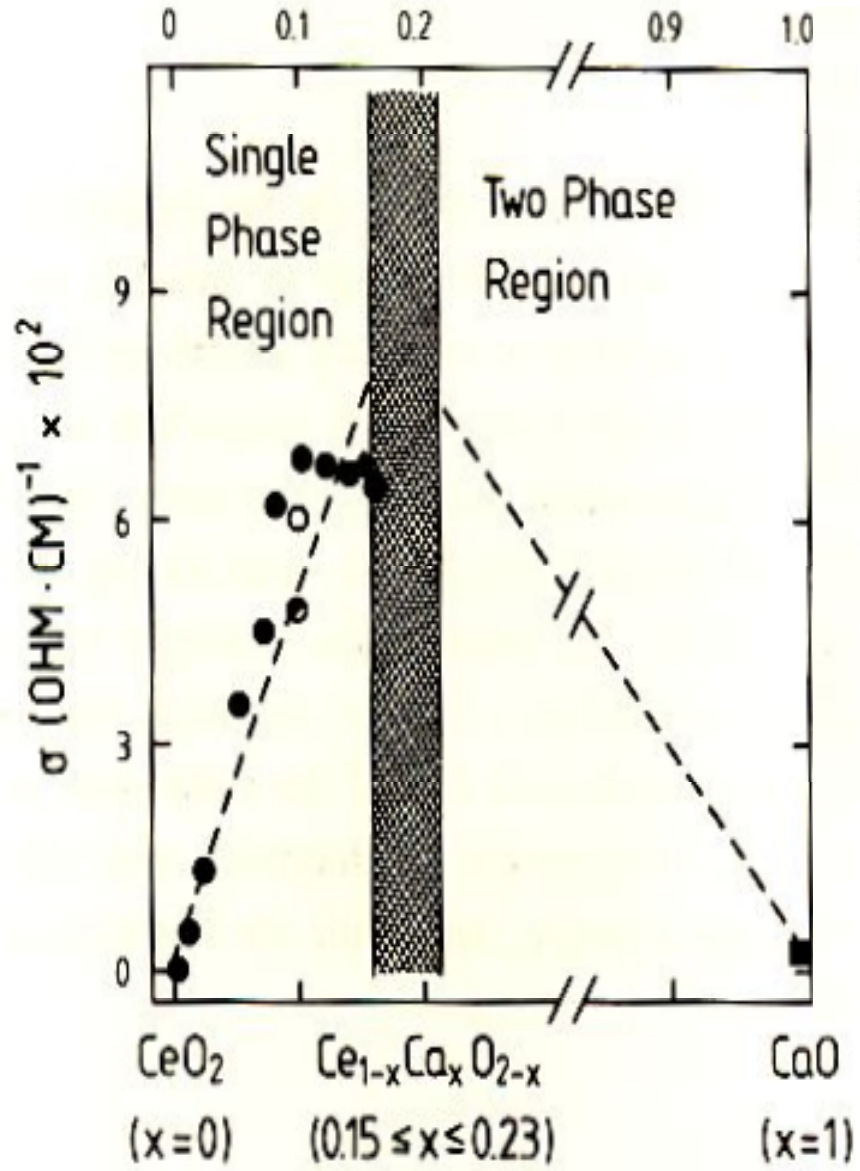
$CH_4 + O_2$

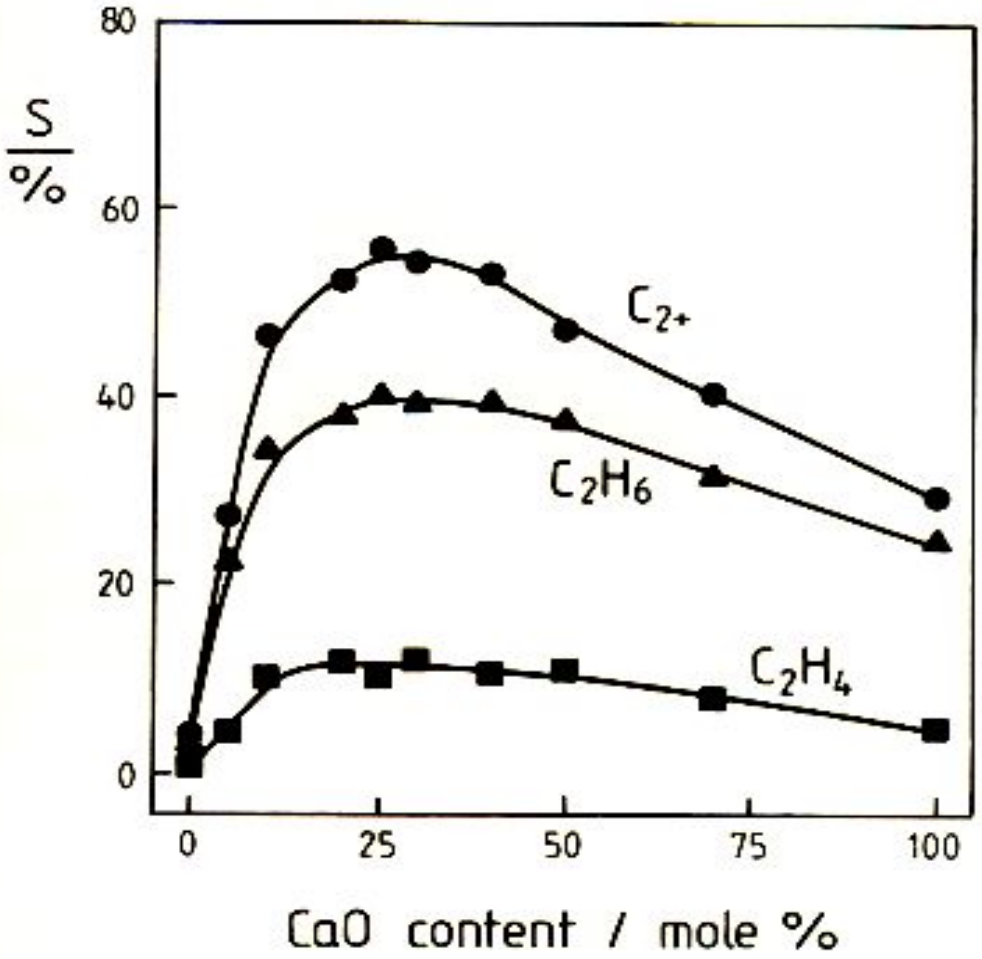


$C_2H_6 + O_2$

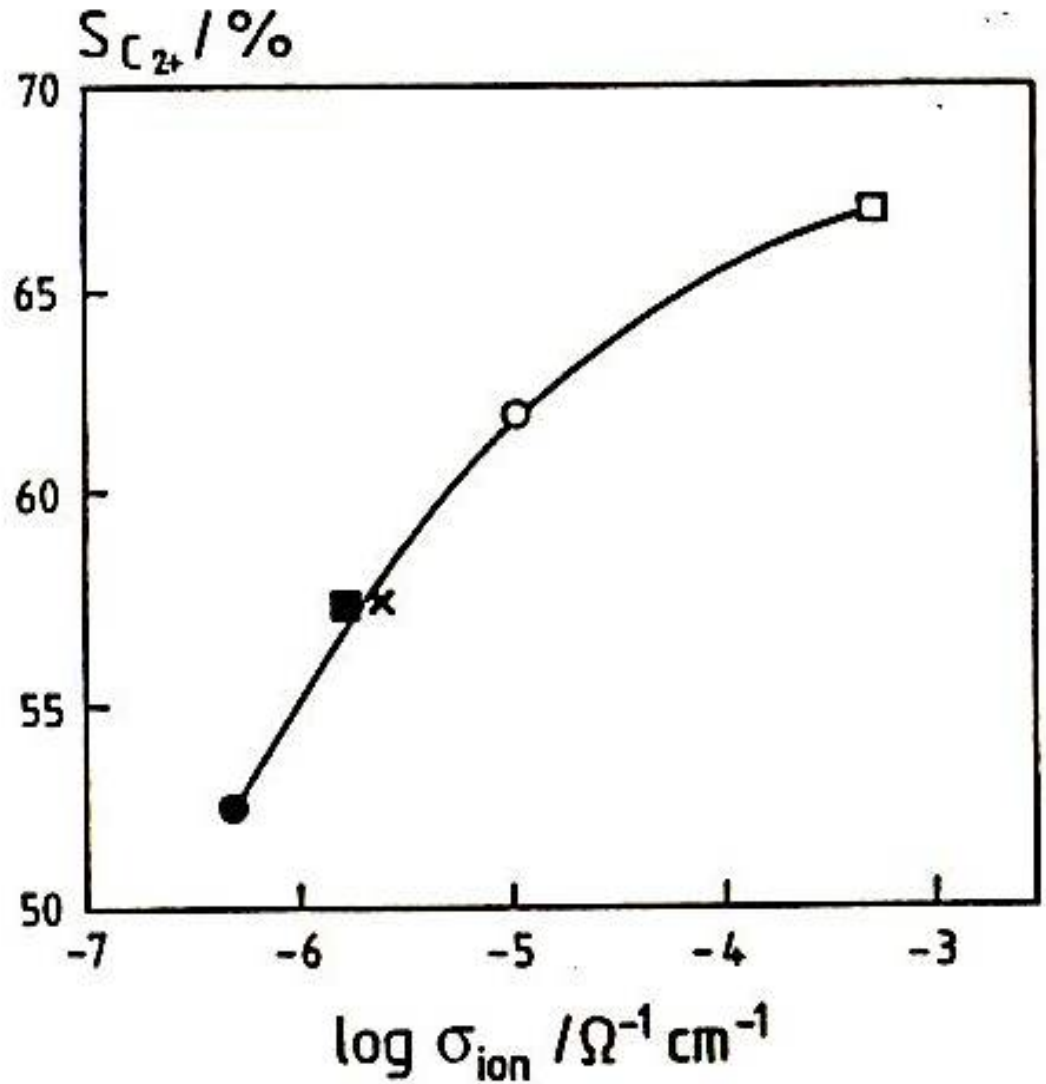


Effect of Composition/Anion Conductivity on Selectivity in OCM over a CeO2/CaO Catalyst





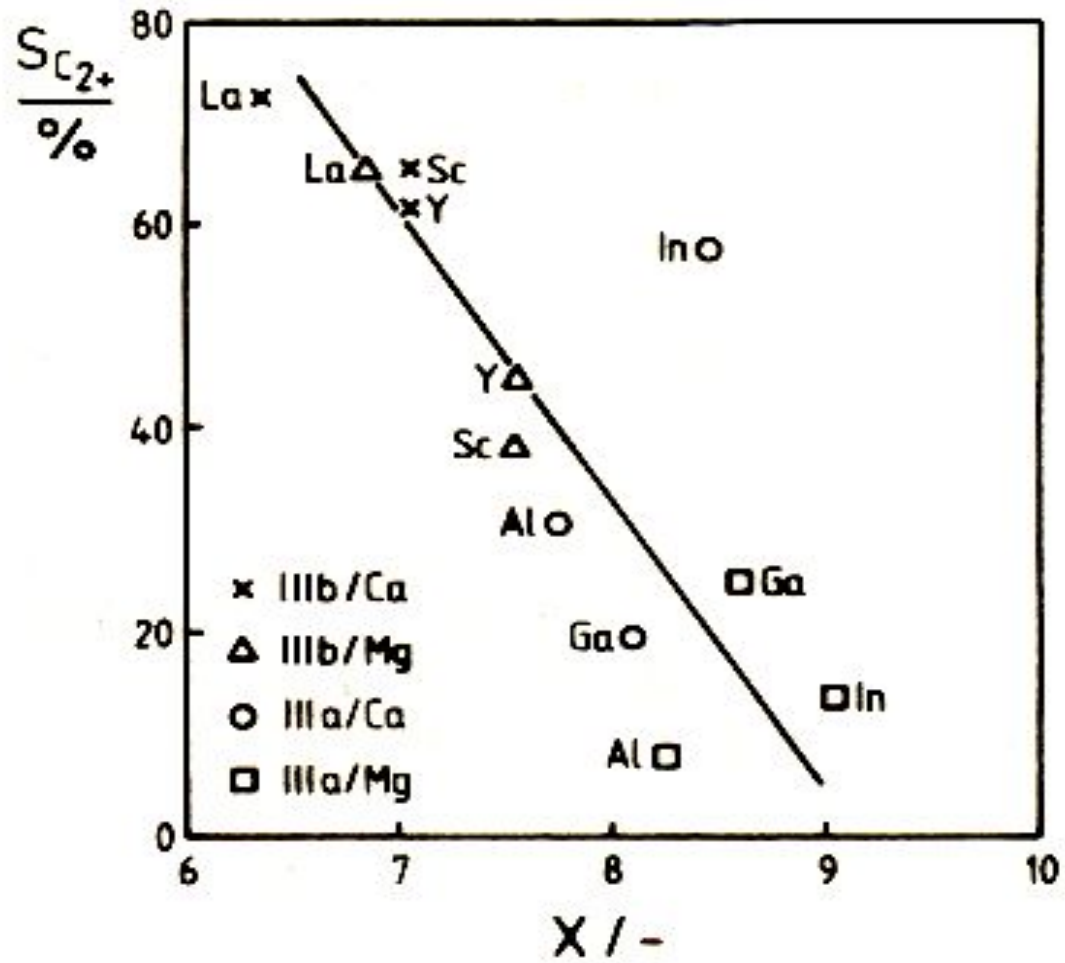
Effect of Anion Conductivity on C_2 Selectivity in OCM Reaction over CeO_2/CaO Catalysts



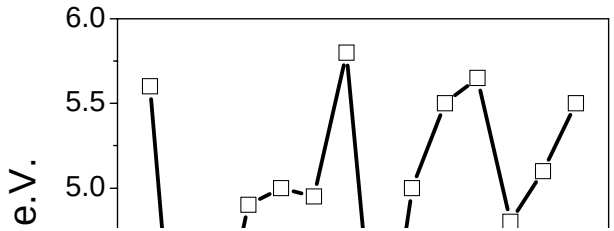
Effect of Oxygen Anion Conductivity on C_2 Selectivity for Different Oxides

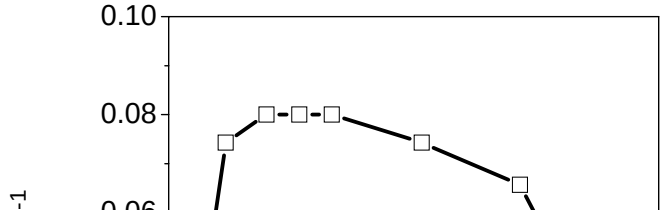
Katalysator	lg σ_{ion} [$\Omega^{-1}cm^{-1}$]	$S_{C_{2+}}$ [%]
ThO_2	−7,06	25
Y_2O_3	−6,91	42
Sm_2O_3	−5,58	45
La_2O_3	−5,67	55
Y_2O_3(5 Mol.-%)/ThO_2	−5,32	54
Sm_2O_3(5 Mol.-%)/ThO_2	−4,31	62
Sm_2O_3(10 Mol.-%)ThO_2	−3,99	62
La_2O_3(10 Mol.-%)ThO_2	−3,52	68
SrO(5 Mol.-%)/La_2O_3(10 Mol.-%)/ThO_2	−3.37	71

Effect of Electronegativity of different Oxides on C_2 Selectivity

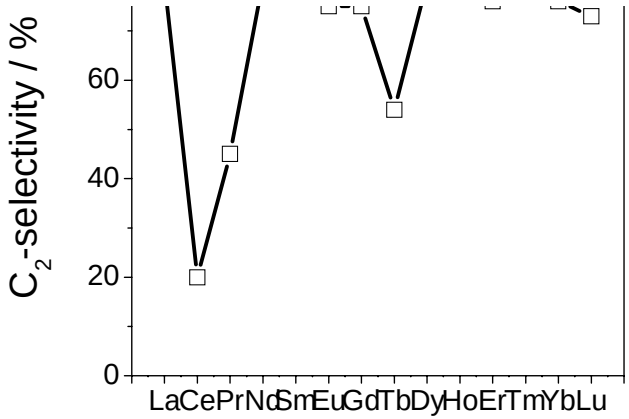


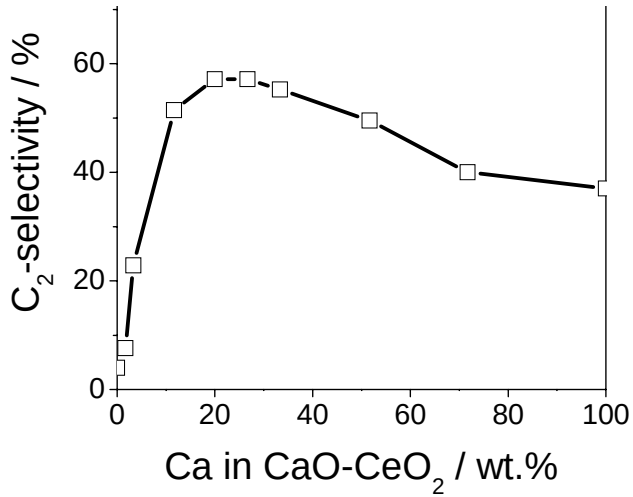
Selectivity-determining factors in OCM
- electronic properties of catalysts -





An optimized ratio of p-type to ionic-type conductivities is required for well-performing OCM catalysts





Scientific Knowledge on the OCM Catalysis

- **Co-feeding of O_2 and CH_4**
  - Basic catalytic materials are considered to be more efficient than the acidic ones (activation of C-H bond)
  - p-type semi-conductors are more selective than n-type ones. Band gap should be in the range of 5-6 eV.
  - An optimal ratio of p-type conductivity to O^{2-}-conductivity is required (fast dissociation of adsorbed bi-atomic O species)
  - Structural point defects (anion vacancies, impurity transitional metal ions)
- **Periodic mode of operation**
  - High catalyst stability under reducing and oxidizing conditions
  - Catalyst ability for storing oxygen and offering high amounts of lattice oxygen
  - Minimal time of catalyst re-oxidation as compared to period of OCM reaction

Concluding Comments to OCM Catalysis

- Inspite of all the extensive knowledge on OCM catalysis scientific breakthroughs are still required.
- Suppression of consecutive total oxidation of ethane and ethylene at high degrees of methane conversion

Yield Y of C_2 ($Y = S \cdot X / 100\ \%$)

Presently Y = 25 - 28 %

- This results in high expenditures for separation and recycle of

C_2H_6 / **C_2H_4** / **CH_4** / (CO_2, CO)

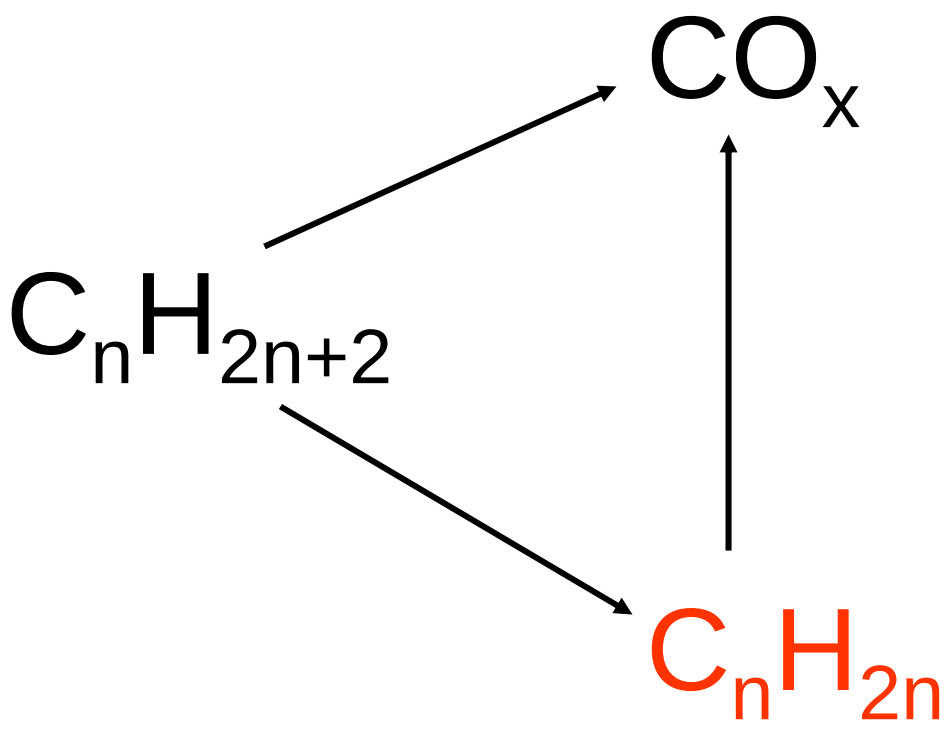
making industrial application uneconomic

Part II

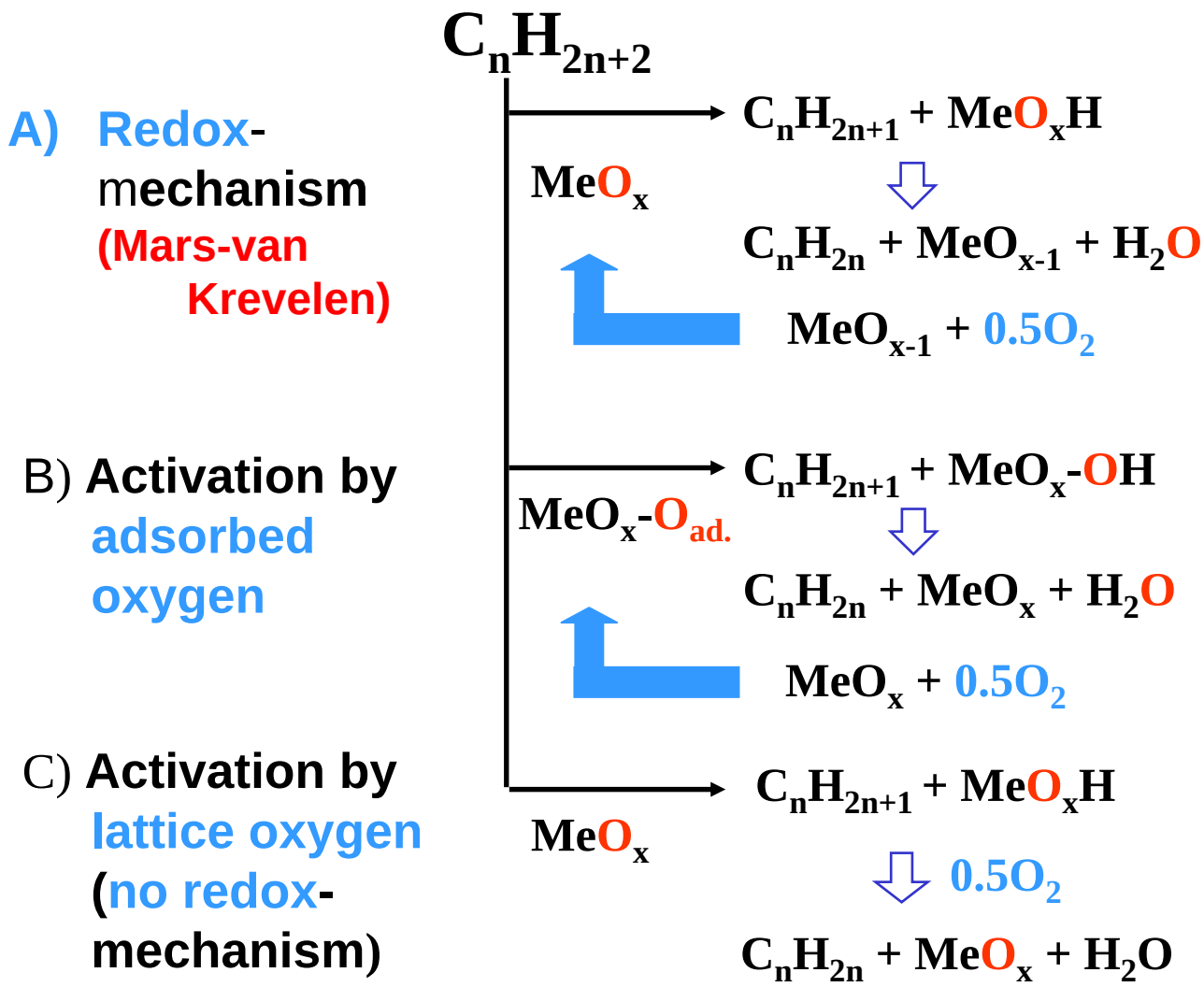
ODP

Oxidative dehydrogenation of propane to propene on different metal oxides (ODP)

Overall Scheme of Oxidative Dehydrogenation of Alkanes to Olefins on Transition Metal Oxides Catalysts

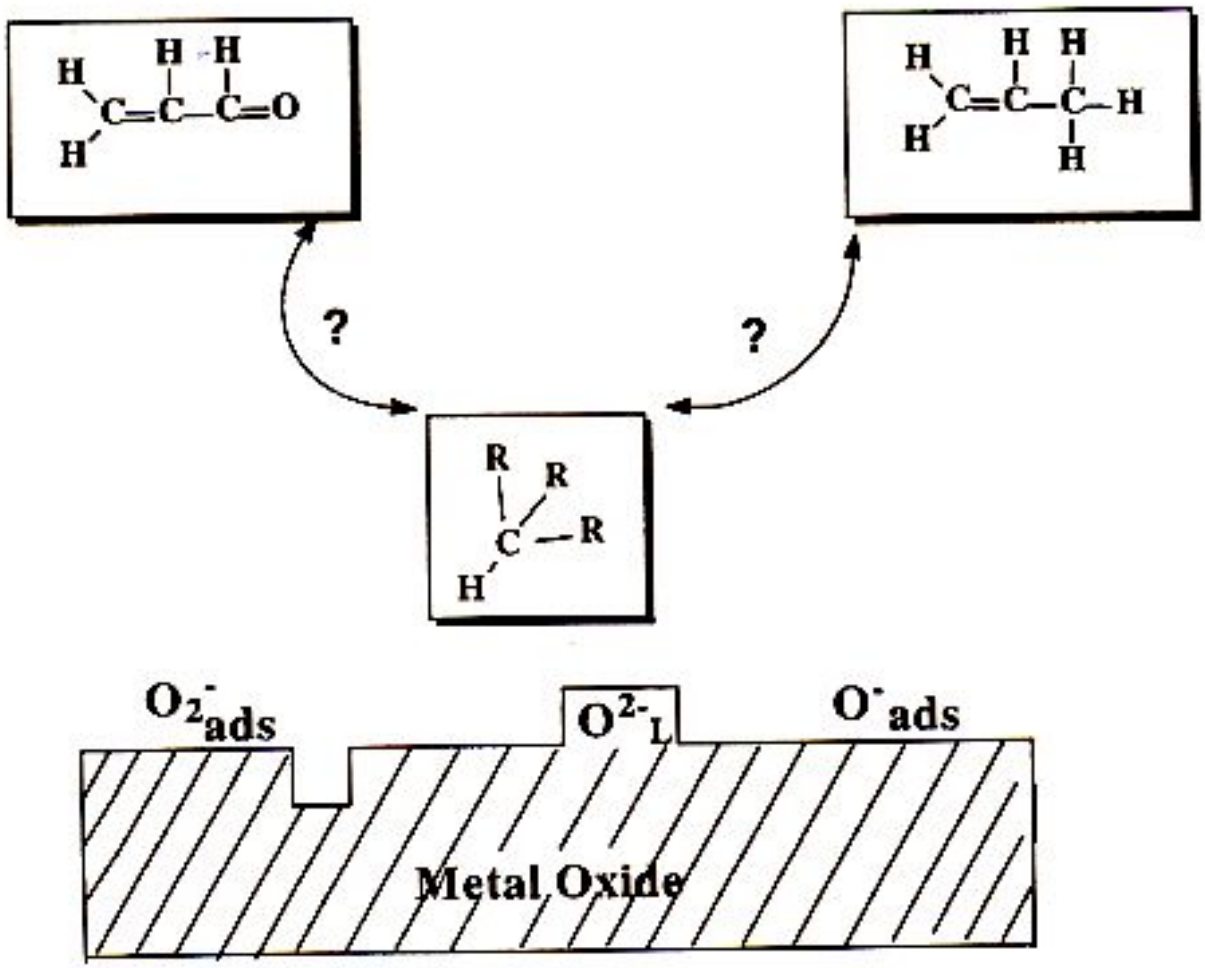


Selection of potential catalysts: Primary reaction steps of the oxidative dehydrogenation of alkanes on metal oxides

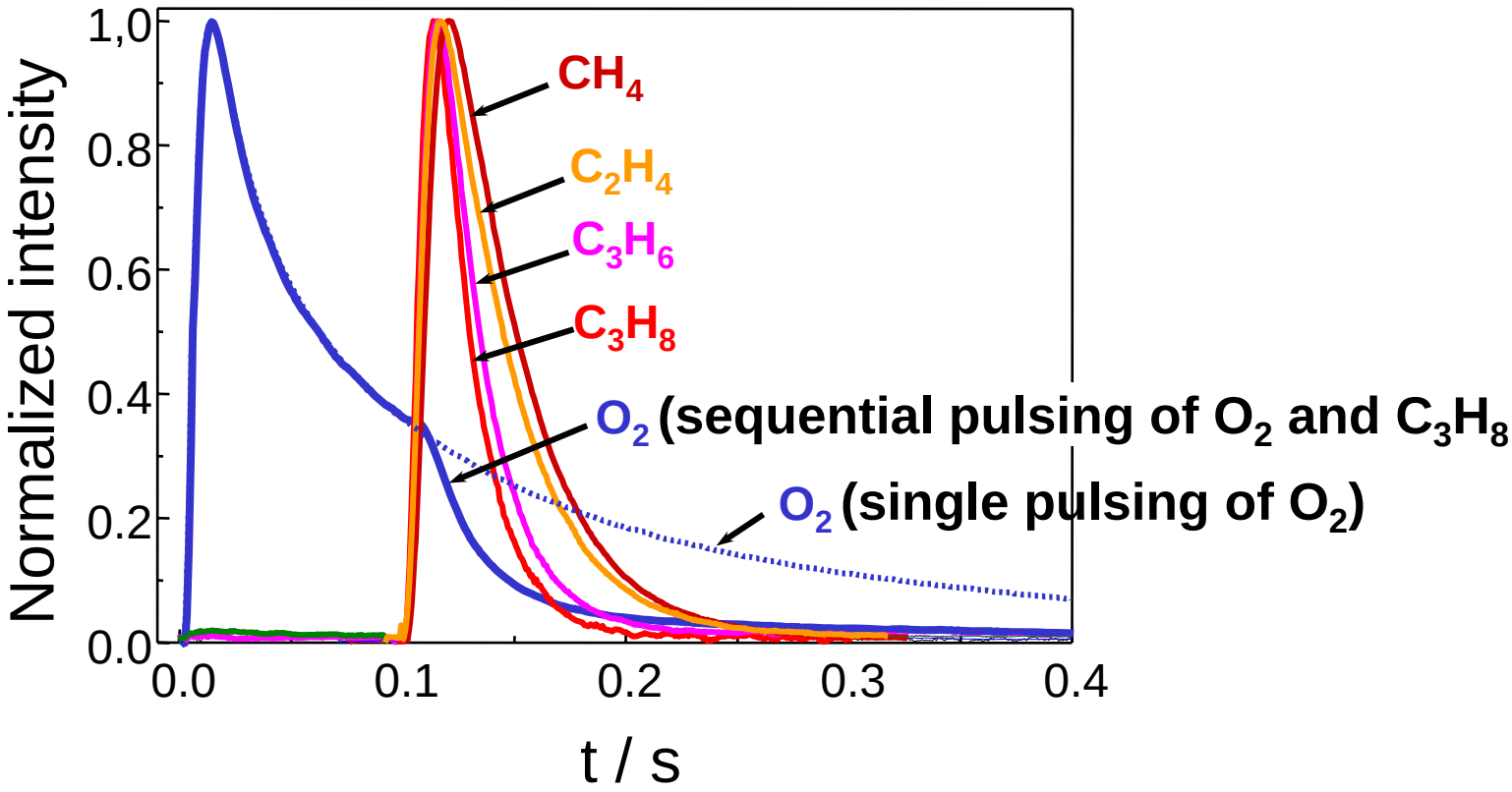


Interactions of an Alkane Molecule with a Catalytic Surface

(different oxygen species)



Propane activation by adsorbed oxygen on $SmNa_{0.028}P_{0.014}O_x$ at 723 K



Reaction of propane with adsorbed oxygen species results in formation of propene followed by its further oxidation to ethylene and methane (besides CO_x)

Catal.Today 42 (1998) 315-323

Complex Mixtures of Metal Oxides as Potential Catalysts for Oxidative Dehydrogenation of Propane

Redox-metal oxides of medium metal-oxygen binding energy in the range –400 to –200 kJ/mol

Redox compounds: **V_2O_5** **Ga_2O_3** **MoO_3**

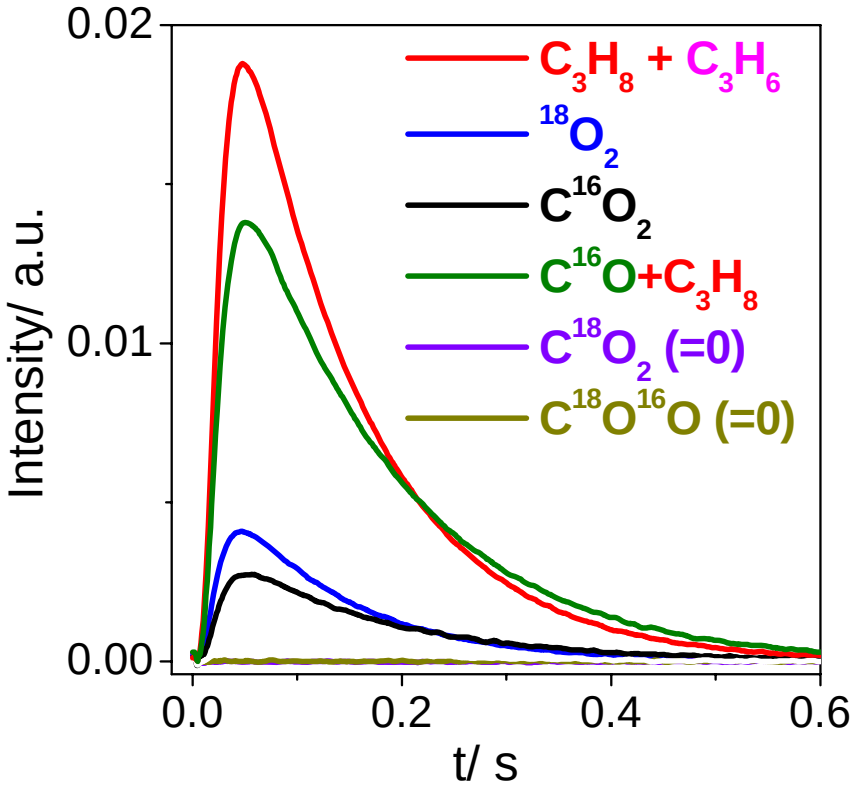
Support: **MgO** (basic metal oxide)

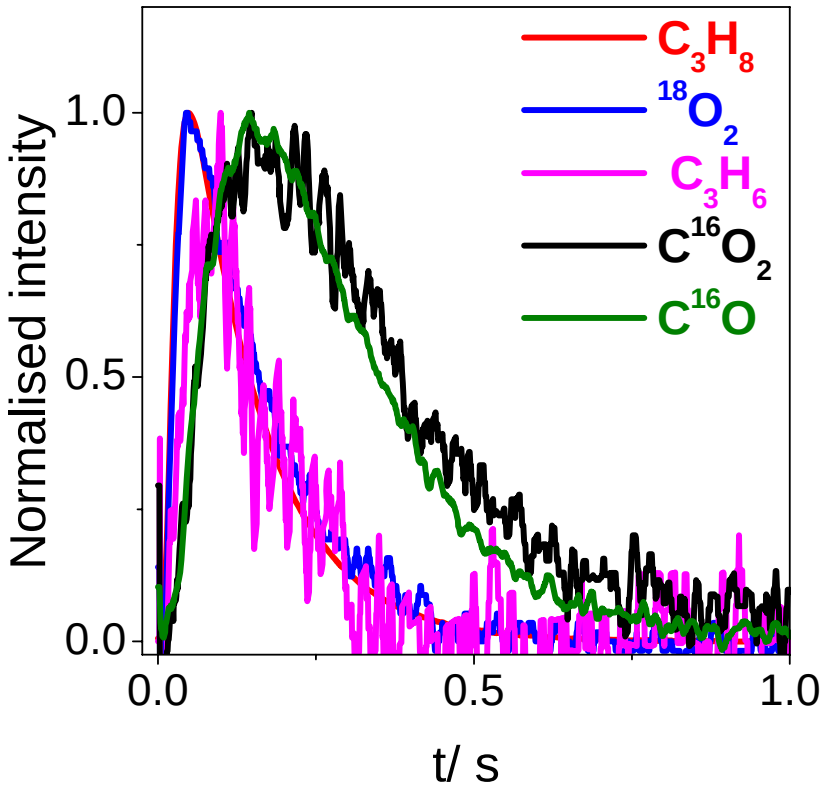
Detrimental to desired catalytic performance

- acidic metal oxide: **B_2O_3**
- metal oxide, on which O_2 dissociates: **La_2O_3**

Propane activation by lattice oxygen

$^{18}O_2$-C_3H_8, $V^{16}O_x$(9.5 %)/γ-Al_2O_3, T=798 K

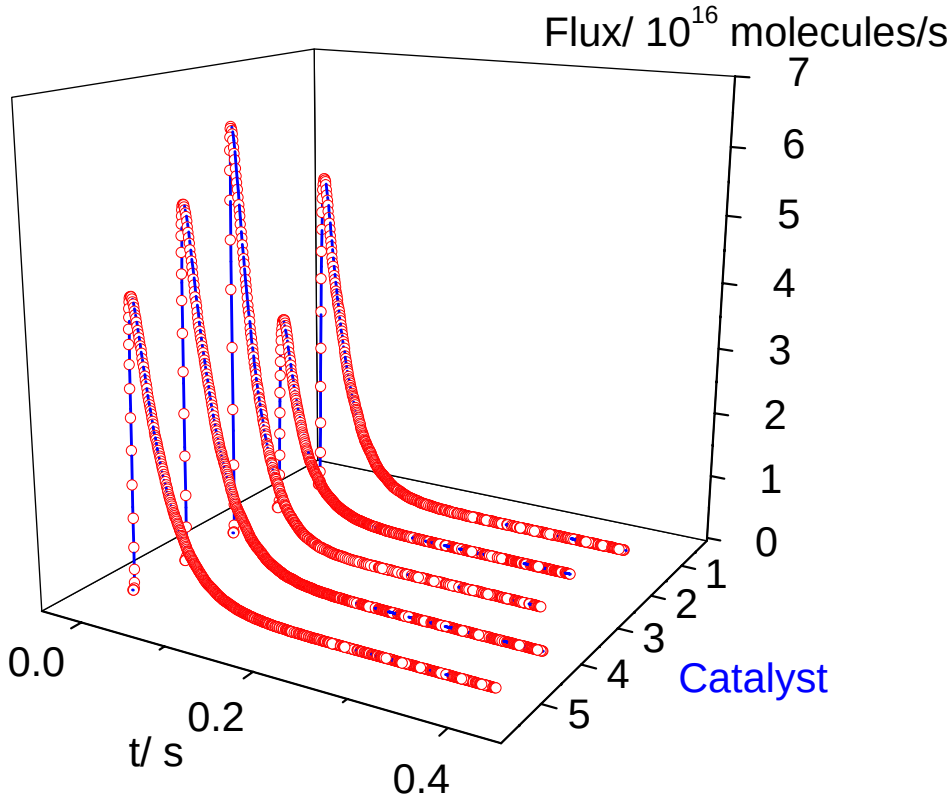




- No labeled (^{18}O) oxygen in CO_x products only lattice (^{16}O) oxygen is involved in the reaction
- Reaction sequence: $C_3H_8 \longrightarrow C_3H_6 \longrightarrow CO$ & CO_2

  MvK mechanism

Kinetic evaluation and mechanistic assessment of oxygen transients



Model for O_2 activation

$$O_2 + 2z \xrightarrow{k_{ads}} 2\,z-O$$

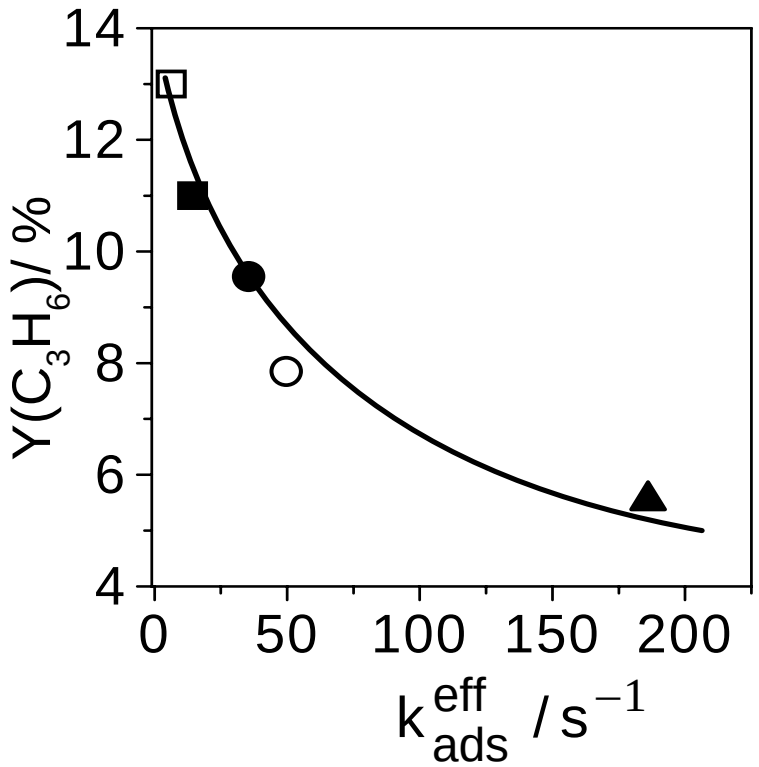
1 $V_{0.16}Mg_{0.11}Ga_{0.47}Mo_{0.17}Fe_{0.09}$
2 $V_{0.32}Mg_{0.18}Ga_{0.27}Mo_{0.04}Mn_{0.19}$
3 $V_{0.8}Mg_{0.2}$
4 $V_{0.2}Mg_{0.8}$
5 $V_{0.22}Mg_{0.47}Ga_{0.2}Mo_{0.11}$

Result: effective rate constant of O_2 activation/adsorption

- rate of formation of active lattice oxygen (regeneration) by gas-phase oxygen
- coverage by active lattice oxygen

Topic.Catal. 15 (2001) 175-180

$Y(C_3H_8)$ versus effective rate constant of O_2 activation determined from TAP experiments



- $V_{0.2}Mg_{0.8}$
- $V_{0.22}Mg_{0.47}Ga_{0.2}Mo_{0.11}$
- $V_{0.32}Mg_{0.18}Ga_{0.27}Mo_{0.04}Mn_{0.19}$
- $V_{0.16}Mg_{0.11}Ga_{0.47}Mo_{0.17}Fe_{0.09}$
- $V_{0.8}Mg_{0.2}$

Steady-state experiments

➡ $Y(C_3H_6)$ decreases with an increase in k_{ads}^{eff}
high concentration of near-surface lattice oxygen facilitates total oxidation

Topics in Catal. 15 (2001) 175-180

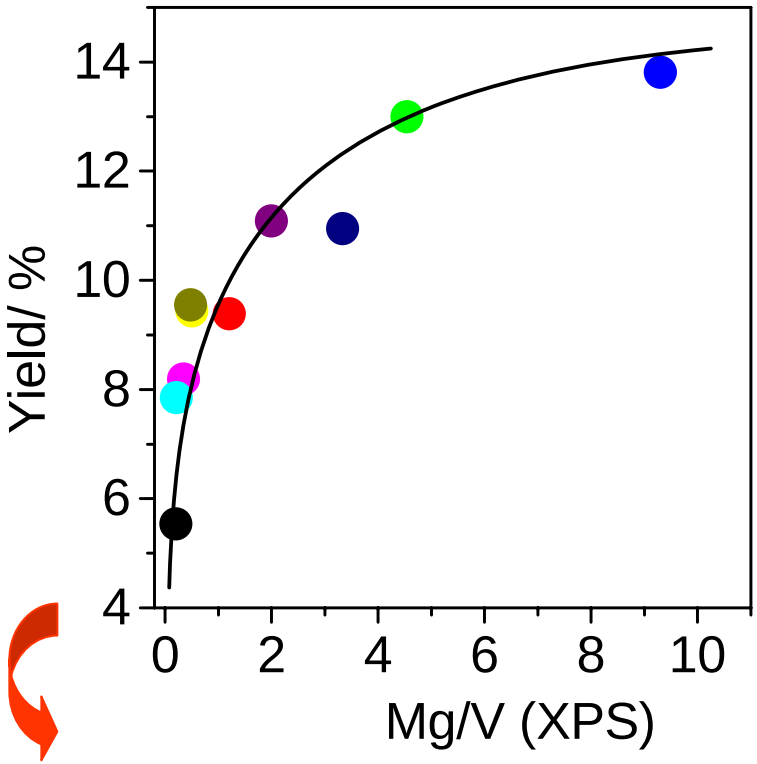
Mechanistic and Kinetic Aspects

- For the ODP reaction on vanadia-based catalysts, transient experiments proved that the dehydrogenation occurs by lattice oxygen via a Mars-van-Krevelen mechanism
- On non-transition metal oxides catalysts adsorbed oxygen plays a major role
- High concentrations of near-surface lattice oxygen as well as of adsorbed oxygen favour total oxidation

Characterisation of catalytic sites of vanadia-based catalysts

XPS & EPR: Relationship between catalytic performance and surface ratio of Mg/V

Reaction conditions: C_3H_8-O_2-N_2=40-20-40; T=773K; X(O_2) ≈100 %



- $V_{0.3}Mg_{0.63}Ga_{0.07}O_x$
- $V_{0.22}Mg_{0.47}Ga_{0.2}O_x$
- $V_{0.32}Mg_{0.18}Mo_{0.04}Mn_{0.09}Ga_{0.33}O_x$
- $V_{0.16}Mg_{0.11}Mo_{0.17}Fe_{0.09}Ga_{0.47}O_x$

} from the evolutionary procedure

- $V_{0.2}Mg_{0.5}Ga_{0.3}O_x$
- $V_{0.2}Mg_{0.2}Ga_{0.6}O_x$

} best from V-Mg-Ga-O/αAl_2O_3

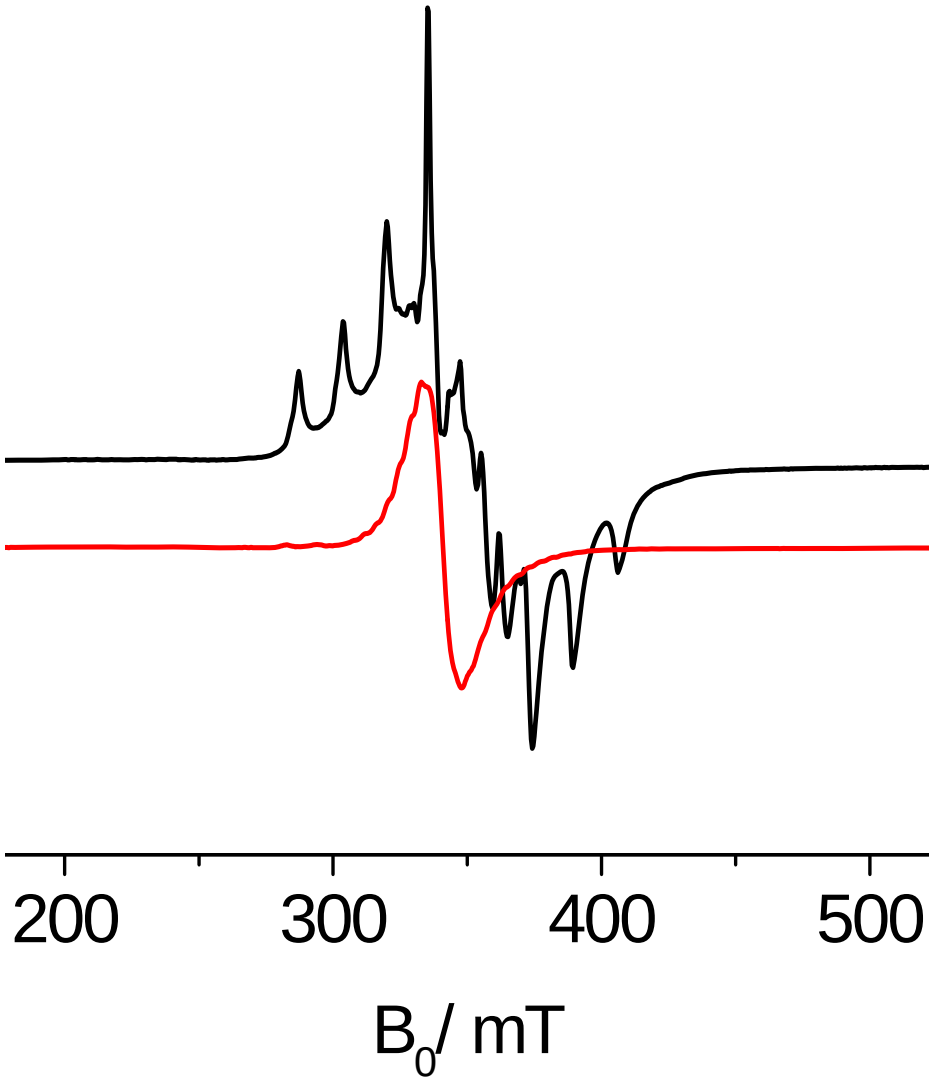
- $V_{0.8}Mg_{0.2}O_x$
- $V_{0.5}Mg_{0.5}O_x$
- $V_{0.2}Mg_{0.8}O_x$
- $V_{0.1}Mg_{0.9}O_x$

} Not supported V-Mg-O

EPR measurements show increasing concentration of octahedral isolated VO^{2+} centres with increasing the Mg/V ratio (XPS). The more dispersed active vanadium species, the higher the selectivity that can be achieved.

Catal.Today 67 (2001) 369-378

EPR Spectra of VMgO catalysts



$V_{0.1}Mg_{0.9}O_x$

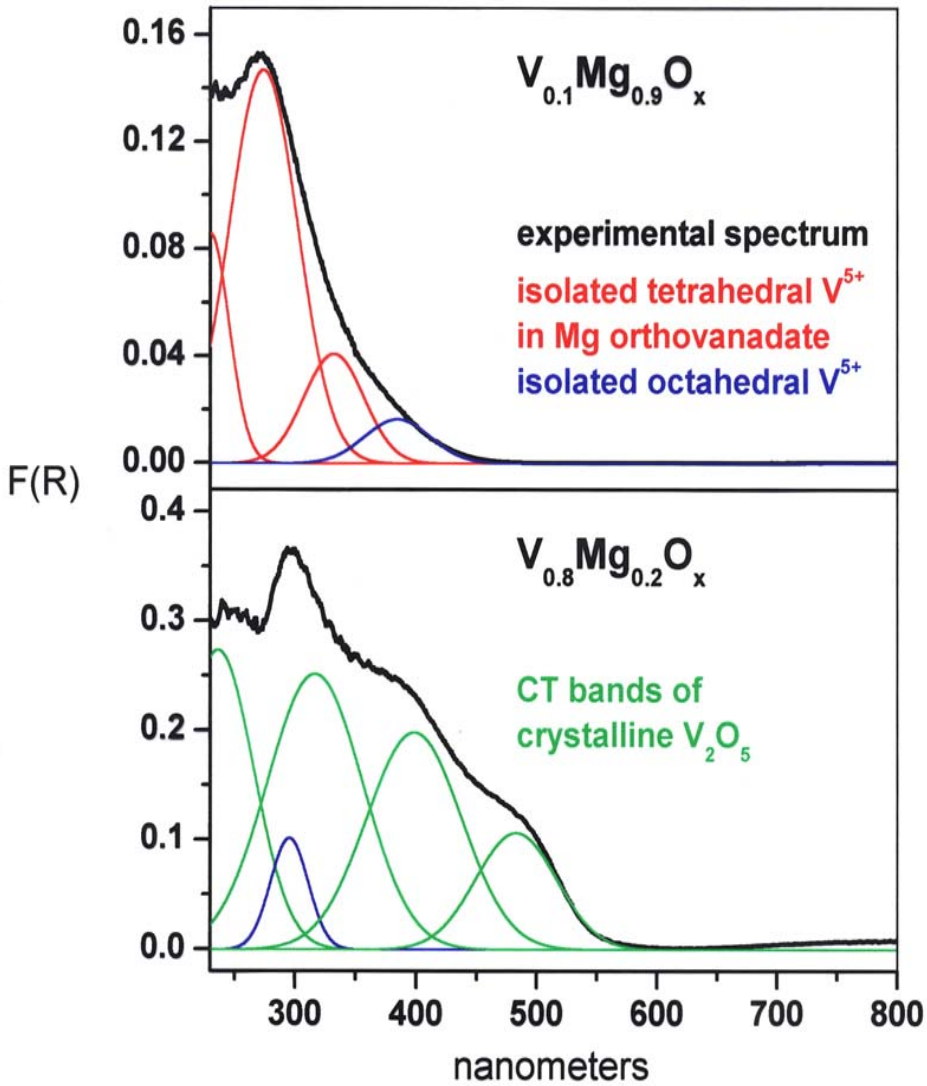
Isolated VO^{2+}

weakly interacting VO^{2+}

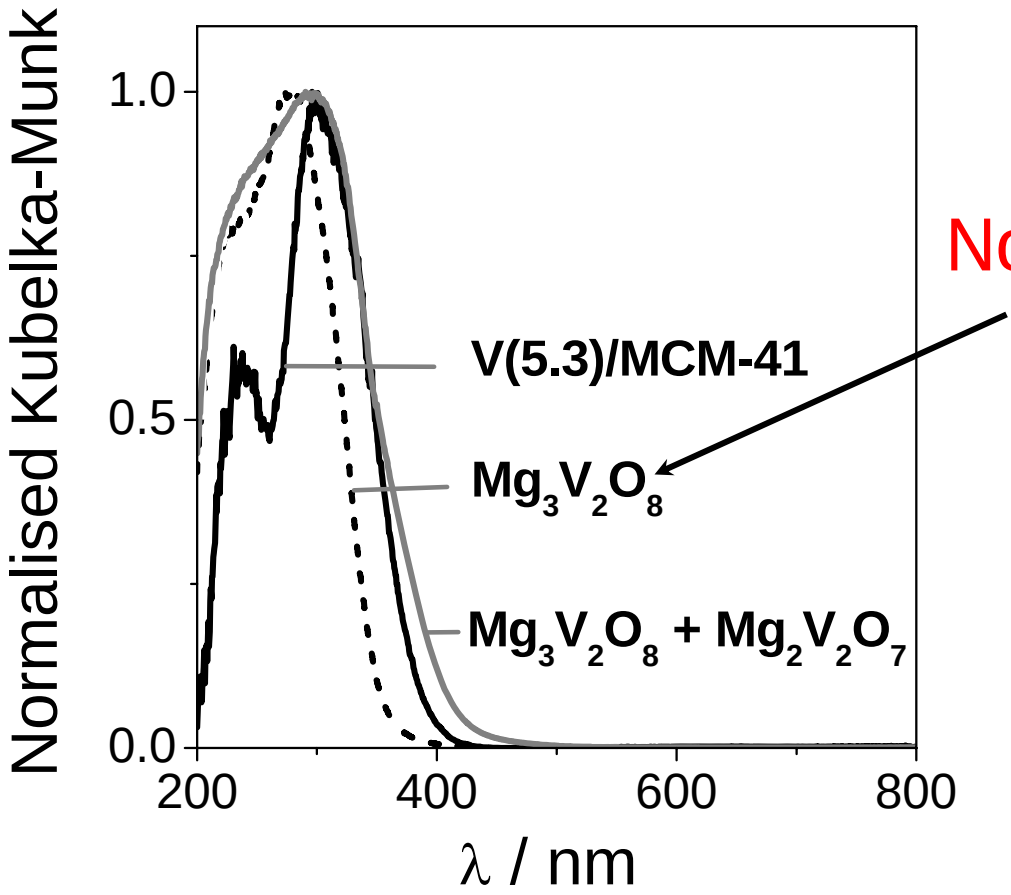
$V_{0.8}Mg_{0.2}O_x$

Strongly interacting VO^{2+}

UV/VIS-DRS spectra of VMgO catalysts



UV-vis spectra: Interaction of VO_x species of different materials at 773 K



No V-O-V bond !

Weak interaction between highly dispersed $V^{5+}O_x$ species

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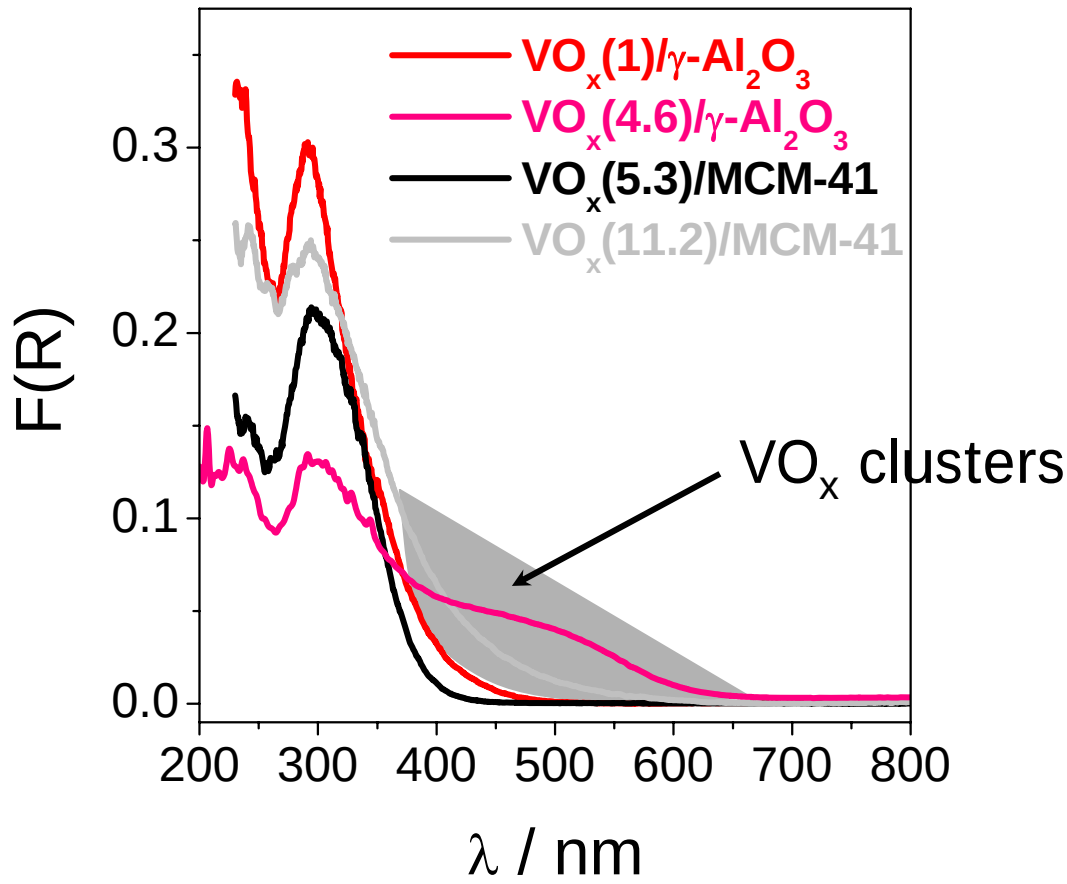
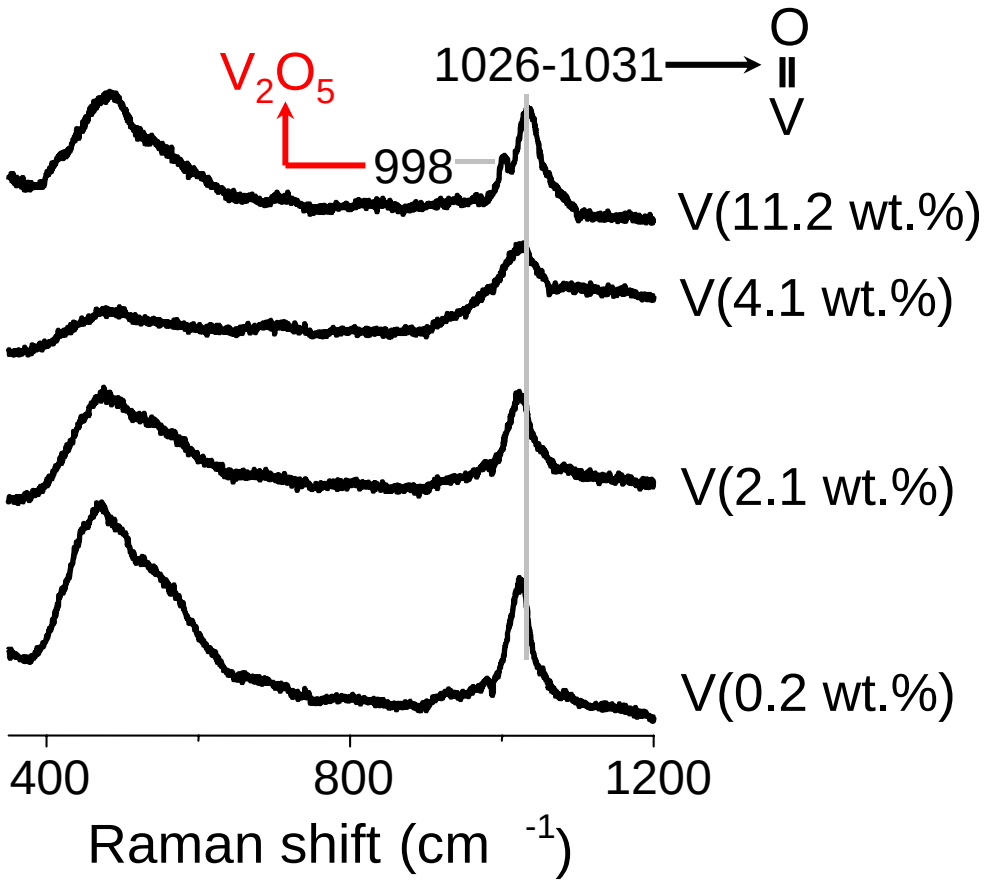
UV-vis spectra: Interaction of VO_x species on different supports at 773 K



Degree of interaction (polymerisation) of $V^{5+}O_x$ is a function of vanadia loading and the support material

Raman spectra: Identification of „sites“ on VO_x-loaded mesoporous MCM-41



- V_2O_5 phase is present at high vanadia loading
- Weakly interacting VO_x species exist under dehydrated conditions for samples with vanadia loading up to 4 to 5 wt.%

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Conclusions for ODP

- **Operando UV-vis as well as EPR and in-situ Raman spectroscopy indicate the presence of highly dispersed vanadia in the form of monomeric and small 2-dimensional VO_x aggregates, which might be partly considered as isolated sites.**

- **The highly dispersed vanadia species contribute to selective oxidation while crystalline nanoparticles favour formation of carbon oxides**

- **Catalyst preparation: For achieving high selectivity of propene supported vanadia catalysts should be designed in such a way that preferentially weakly interacting VO_x species and preferably isolated sites are prepared.**

- **Reaction conditions: The concentration of near-surface lattice oxygen as well as of adsorbed oxygen should be low to avoid non-selective oxidation.**

What can be learnt?

From Elucidation of catalysis

→ improvement in

- understanding of interaction between reactant and catalyst
- catalyst development and optimization

From Kinetics of catalytic reaction

→ improvement in

- understanding of mechanistic aspects
- catalytic reaction-engineering procedures

References for further reading on hydrocarbon oxidation catalysis

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The End