Applied CAtalysis

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Oxidation of 1-butene and n-butane: an alternative route to acetic acid

MAX-PLANCK-GESELLSCHAFT

AC FHI

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WACKER

Background

- ✓ Alternative technology of production of acetic acid (AA): oxyhydrative scission (OHS) of n-C_4 hydrocarbons over VO_x/TiO_2 catalysts [1] for medium size plants developed by Consortium für elektrochemische Industrie [2]
- ✓ Main reactions:

$$C_4H_{10} + 2{,}5\ O_2 \longrightarrow 2\ CH_3COOH + H_2O$$

$$C_4H_8 + 2\ O_2 \xrightarrow{H_2O} 2\ CH_3COOH$$

- ✓ Cyclic process: p = 10 bar, T = 200 °C
- ✓ Side products: propionic acid, formic acid (FA)

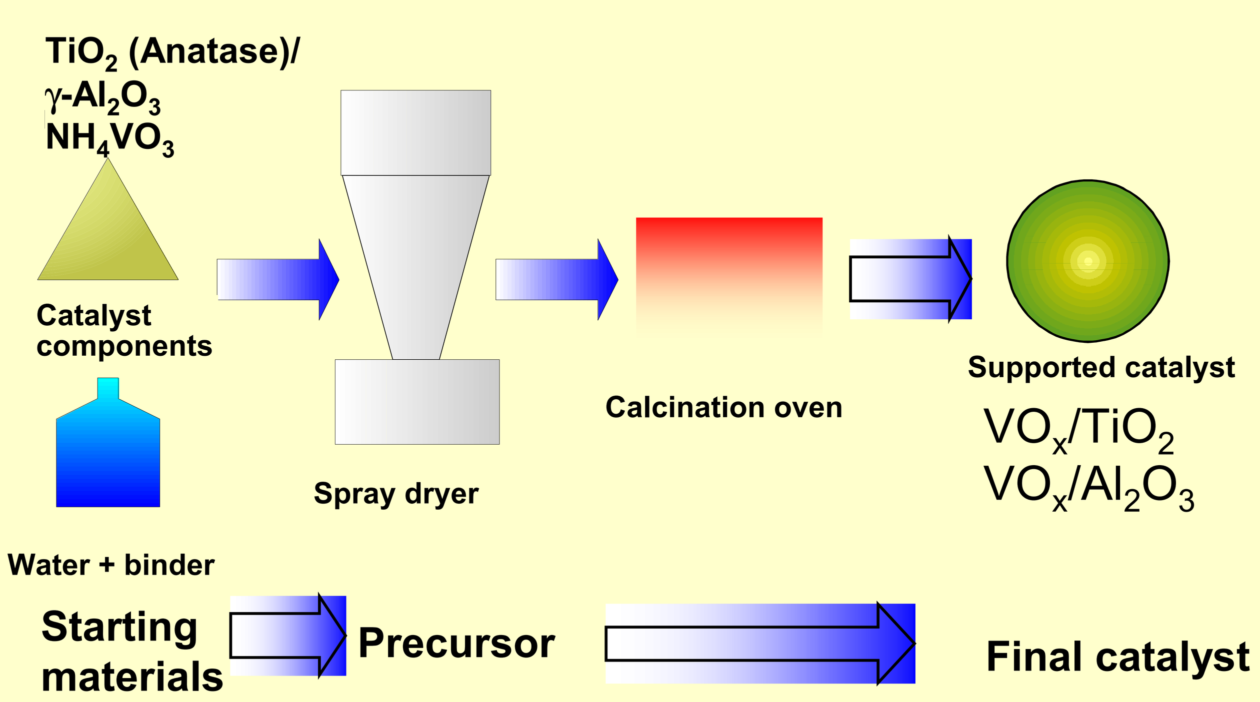
Aims

- ✓ Enhancement of the selectivity to AA by improvement of the catalyst
- ✓ Optimisation of the catalytic reaction conditions
- ✓ Increase in productivity in the oxidation of n-butane

Approach

- ✓ Variation of support material (TiO_2 vs. Al_2O_3)
- ✓ Adding of different dopants
- ✓ Variation of vanadia loading
- ✓ Variation of reaction conditions (pressure of reaction, water content of the feed)
- ✓ Once-through investigations (1-butene, n-butane)

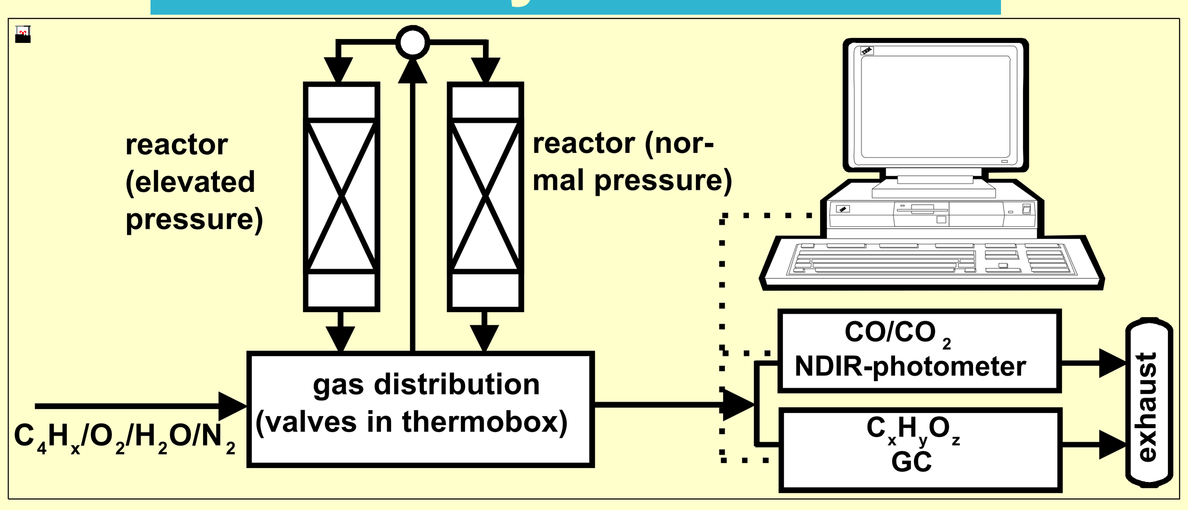
Catalyst preparation



Catalyst characterisation

sample	support	w/ wt.-% V	Mo	Sb	S_{BET}/ $m^2\ g^{-1}$
A	TiO_2	6.08	–	–	79
B	TiO_2	5.13	1.71	–	77
C	TiO_2	4.19	–	9.53	74
D	Al_2O_3	6.60	–	–	55

Catalytic tests



- ✓ Once-through mode in two fixed bed reactors
- ✓ On line process monitoring (GC, NDIR)
- ✓ Standard feed: 1.9 % C_4/9.1 % O_2/24.4 % H_2O/N_2

Normal pressure / butene

Effect of dopants and supports

Dopant	Catalyst	S(AA)	S(AcH)	S(FA)	T
„without"	A (TiO_2)	54	7	6	155
Mo	B (TiO_2)	55	12	6	155
Sb	C (TiO_2)	65	15	1	148
Sb	D(Al_2O_3)	46	15	1	185

S (%) and T (°C) at 15 % butene conversion, p= 1 bar, standard feed, GHSV(NPT) = 3730 h^{-1} (TiO_2), 200 h^{-1} (Al_2O_3)

AA: acetic acid, AcH: acetaldehyde, FA: formic acid

- ✓ Increase in selectivity to AA und AcH in the order „without" < Mo < Sb
- ✓ VO_x/Al_2O_3 is less active und less selective than VO_x/TiO_2

Effect of vanadia loading

sample	c(V)/%	c_{spez}(V)/%m^{-2}	X(butene)	S(AA)	S(AcH)	S(FA)
T1	1.1	0.02	25	37	5	6
T3	3.3	0.05	37	58	10	5
T5	4.7	0.06	40	54	7	6
T10	9.7	0.12	39	60	10	5
T14	14.0	0.24	37	53	7	6

m_{Kat} = 0,7 g, GHSV: 3730 h^{-1}, T = 180°C, standard feed, p = 1 bar

- ✓ High catalyst performance for loadings > 0.05 % V m^{-2} (= 0.11 % V_2O_5 m^{-2})
- ✓ Corresponds to an approximate minimum coverage a half a theoretical monolayer [3]

Conclusions

✓ **Catalyst composition**

- VO_x content on TiO_2: minimum of 0.05 % V m^{-2} necessary for the formation of catalytic highly effective VO_x/TiO_2 surface structures
- Doping with appropriate oxides, e.g. Sb_2O_3: Increase in activity and selectivity and enhancement in yield of AA

✓ **Support material**

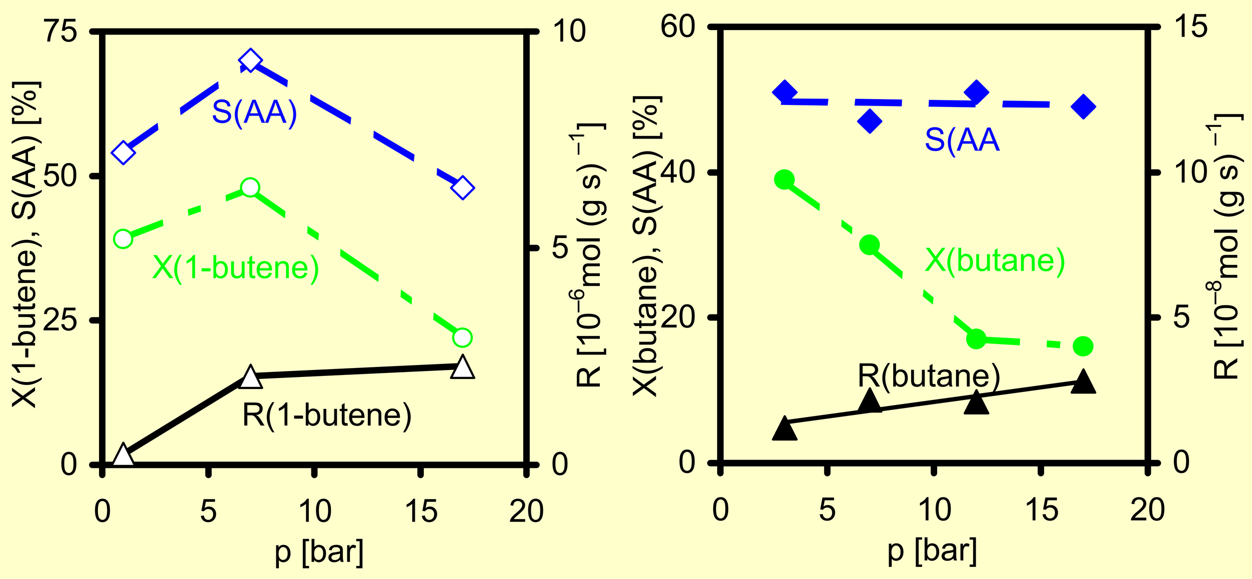
- redox active TiO_2 (anatase) better suited than redox *inactive* γ-Al_2O_3, support is thought to take part in catalytic reaction

✓ **Effect of reaction conditions**

- optimum conditions are different for the both substrates
- butene is siuted as model reactant for butane only for specific constraints

Effect of pressure

1-butene / n-butane

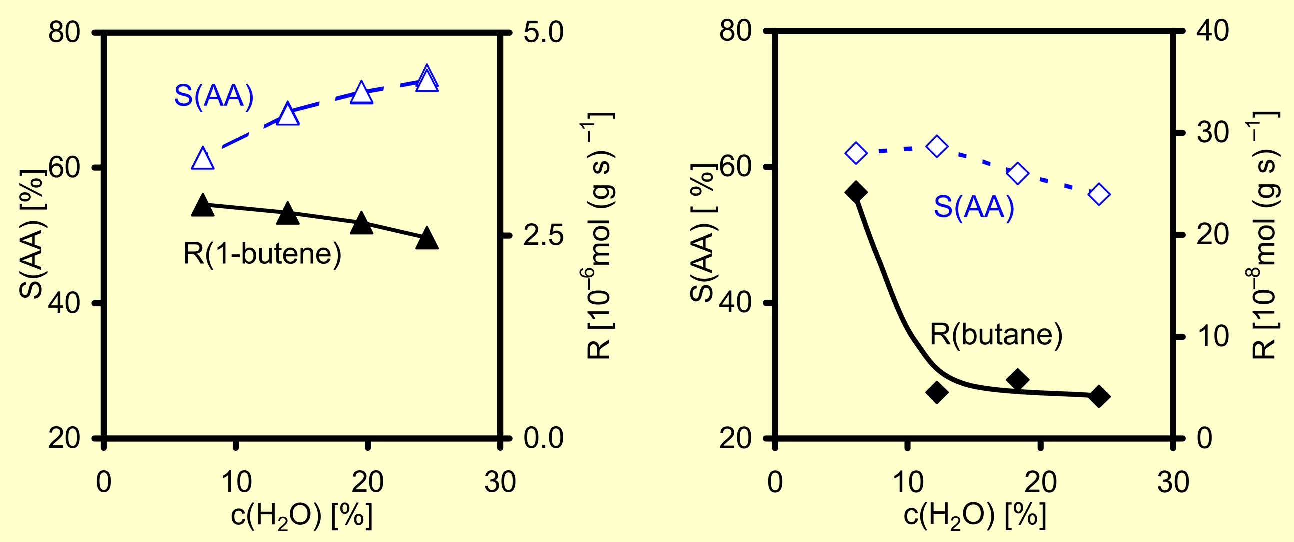


Catalyst: C, GHSV(NPT): 3730 h^{-1} (butene), 74 h^{-1} (butane), T = 180 °C, standard feed

- ✓ Butene: maximum of conversion and AA select. at 7 bar
- ✓ Butane: with increasing pressure: conversion degree decreasing, AA select. constant

Effect of water content in feed

1-butene / n-butane



Catalyst: C, GHSV(NPT): 3730 h^{-1}=const. (butene); adjusted to 20 % conversion (butane), T = 185 °C, p = 7 bar, standard feed

- ✓ Marked differences in activities and AA selectivities in butene and butane oxidation for kinetic reasons

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