From a kinetic analysis to an advanced performance of highly dispersed VO$_x$-species in conversion of C$_3$-C$_4$ alkanes to olefins

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Articles


2) O. Ovsitser, and E.V. Kondratenko, “Similarity and differences in the oxidative dehydrogenation of C\textsubscript{2}-C\textsubscript{4} alkanes over nano-sized VO\textsubscript{x} species using N\textsubscript{2}O and O\textsubscript{2}“ Catal. Today, 142 (2009) 138-142.


4) O. Ovsitser, M. Cherian, A. Brückner, and E.V. Kondratenko, ”Dynamics of redox behavior of nano-sized VO\textsubscript{x} species over Ti-Si-MCM-41 from time-resolved in-situ UV/Vis analysis“, J. Catal., 265 (2009) 8-18.

Publications and presentations 2009-2010

Talks

1) E.V. Kondratenko
"Using time-resolved methods to monitor and understand catalytic oxidation reactions"
plenary lecture at 6th World Congress on Oxidation Catalysis, Lille, France, 05-10.07.2009.

2) E.V. Kondratenko
"Mechanistic insights into the role of oxidant in catalytic conversions of small molecules"
Festkolloquium anlässlich des 75. Geburtstages von Professor Manfred Baerns, 23.09.2009, Rostock, Deutschland

3) E.V. Kondratenko
"Catalytic removal of nitrogen oxides. A mechanistic view from transient experiments"
Seminar at the Institute of Technical Chemistry, University of Leipzig, Germany, 05.05.2009.
Background and materials

Selectivity and activity of VO$_x$ aggregates in ODH strongly depends on:

- their structure
- surface density
- reaction conditions

$\text{VO}_x$(2-11 wt.%)/MCM-41(Ti/Si=0-1.5), $\text{VO}_x$(1-5 wt.%)/$\text{SiO}_2$

Can we force $\text{VO}_x$ species to work selective at high degrees of alkane conversion?

V surface density $\sim 0.4 - 0.7$ V/nm$^2$
(< 5-10% of V monolayer)
Experimental: Catalytic tests

Oxidative dehydrogenation of C\textsubscript{2}-C\textsubscript{4} alkanes

Broad range of operation conditions:

\[ P_{\text{total}} = 1 \text{ bar}, T = 673-873 \text{ K} \]

\[ C_nH_{2n+2} : O_2 : \text{Ne} = (5-100) : (0-20) : (1-40) \]

\[ C_nH_{2n+2} : N_2O : \text{Ne} = (5-100) : (0-40) : (1-20) \]

Strong variation of oxidant content!

\[ C_3H_8 + (O_2, N_2O) \rightarrow C_3H_6 \]

iso-\[C_4H_{10} + (O_2, N_2O) \rightarrow \text{iso-}C_4H_8 \]
Experimental: Characterization

**in situ-UV/Vis**

- Isotopic label 1 or reducing agent
- Isotopic label 2 or oxidizing agent
- Quartz reactor
- Movable thermocouple
- Optical fibres
- Real catalyst bed
- UV/Vis
- Control (X, S)
- Quartz particles
- QMS and GC

**Technical data**

- T up to 1073 K, P up to 15 bar, Fast UV/Vis analysis (every 1 s)
- On-line MS analysis, Fast valves for transient analysis

**Graphs**

- Kubelka-Munk / a.u.
- Concentration / vol.%

**Equations**

- Oxidised in O$_2$
- After 25 s in C$_3$H$_8$
- After 100 s in C$_3$H$_8$
- After 320 s in C$_3$H$_8$

SFB 546 „Übergangsmetalloxid-Aggregate“ Teilprojekt B3 (Kondratenko/Schomäcker)
Correlation of catalyst selectivity and kinetic data

The reduction degree of VO$_x$ species is an important selectivity-governing factor

Influence of \( \text{O}_2 \) and \( \text{N}_2\text{O} \) on catalytic performance of highly dispersed \( \text{VO}_x \) species in ODH reactions of \( \text{C}_3\text{-C}_4 \) alkanes

\[ T = 773 \text{ K}; \text{ same O-atoms content: } C_n\text{H}_{2n+2}: \text{O}_2: \text{Ne} = 40:20:40; C_n\text{H}_{2n+2}:\text{N}_2\text{O}:\text{Ne} = 40:40:20 \]

Nature of oxidant (\( \text{O}_2 \), \( \text{N}_2\text{O} \)) strongly influences the activity and selectivity of \( \text{VO}_x \) species in ODH reactions
Influence of oxidant (concentration) on catalytic performance of highly dispersed \( \text{VO}_x \) species in ODH of iso-butane

Key aim is to improve olefin selectivity

Can we minimized undesired \( \text{CO}_x \) formation further by variation of oxidant concentration? At high degree of alkane conversion...

Industrially interesting area

\( \text{CO}_x \) formation - decreases the olefin yield
- significantly dilutes outlet gasses
Improving process selectivity of highly dispersed VO$_x$ species in ODH of iso-butane

VO$_x$(5)/MCM-41, $T = 773 - 833$ K

Selectivity to iso-butene can be significantly improved by reducing the oxidant content!

$K(\text{reoxidation})/K(\text{reduction}) > 1$, but $[O_2] << [C_4H_{10}]$

$K(\text{reoxidation})*[O_2]/K(\text{reduction})* [C_4H_{10}] < 1$

High reduction degree

alkene (high) CO$_x$ (low)

Improving process selectivity of highly dispersed VO\textsubscript{x} species in ODH of iso-butane

\[ T = 833 \text{ K}; \quad \text{W/F}=5 \text{ g s ml}^{-1} \text{ for } \text{VO}_{x}(5)/\text{MCM-41} \text{ and } \text{W/F}=15 \text{ g s ml}^{-1} \text{ for } \text{VO}_{x}(11)/\text{MCM-41} \]

\[ \text{iso-C}_{4}\text{H}_{10}: -15 \text{ %}. \]

Amount of iso-C\textsubscript{4}H\textsubscript{8} formed >O\textsubscript{2} passed in RM + O-in VO\textsubscript{x}-species

Contribution of non-oxidative dehydrogenation?
- Yes. H\textsubscript{2} formation was confirmed by GC-analysis with Ar-carrier gas

Contribution of thermal dehydrogenation?
- No. At the same conditions \( X_{\text{iso-C}_{4}\text{H}_{10}} < 0.3 \) % over quartz.

-Catalytic formation of olefins over VO\textsubscript{x}-species.

Samples with highly dispersed VO\textsubscript{x}-species (e.g. VO\textsubscript{x}(5)/MCM-41) have shown best results
Improving process selectivity of highly dispersed $\text{VO}_x$ species in ODH of iso-butane

Comparison of our results with literature data

Can selectivity to propene in propane ODH be also improved by operation at oxygen-lean condition?

Oxygen lean conditions ($\text{iso-C}_4\text{H}_{10}/\text{O}_2 > 10$)
Improving process selectivity of highly dispersed VO$_x$ species in ODH of propane

Comparison of our results with previous data

$S\left(\text{C}_3\text{H}_6\right)/\%$

$X\left(\text{C}_3\text{H}_8\right)/\%$

$\text{C}_3\text{H}_8/\text{O}_2/\text{Ne} = 40/20/40$

$\text{VO}_x(2.7)/\text{MCM-41}$

$\text{VO}_x(2.7)/\text{SiO}_2$

$\text{VO}_x(3.4)/\text{MCM-48}$

$\text{VO}_x(2.7)/\text{SBA-15}$

*B2 Hess C, Schlögl R.

Improving process selectivity of highly dispersed $\text{VO}_x$ species in ODH of propane

Comparison of our results with previous data

Selectivity to propene can be significantly improved as well by reducing of oxidant content!


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Improving process selectivity of highly dispersed VO$_x$ species in ODH of propane

Comparison of our results with previous data and best literature data

S$_x$(C$_3$H$_6$)/% vs. X(C$_3$H$_8$)/%

Oxygen lean conditions (C$_3$H$_8$/O$_2$ >10)

Cycling conditions: O$_2$-C$_3$H$_8$-O$_2$^*

X(C$_3$H$_8$)=44, S(C$_3$H$_6$)=81%

Selectivity to propene can be significantly improved as well by reducing of oxidant content!

Improving process selectivity of highly dispersed VO$_x$ species in ODH of propane

Stable catalytic performance was achieved over VO$_x$-species in propane dehydrogenation as well!

Formation of olefins over VO$_x$-species:

i) oxidative dehydrogenation during first minutes of operation under oxygen-free or oxygen-lean conditions,

ii) non-oxidative dehydrogenation of alkanes to olefins and hydrogen.

Their relative contribution to the overall olefin production depends on reaction condition (temperature, contact time) and oxygen content in reaction feeds.

Recent papers confirm that considerable amounts of H$_2$ are produced under conditions of propane ODH, with vanadium oxide-based catalysts *, **

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Improving process selectivity of highly dispersed VO$_x$ species in ODH reactions of C$_2$-C$_4$ alkanes

TPO VO$_x$(1.3%)/SiO$_2$ (after 24 hours TOS in propane DH)

At optimal operation conditions formation of carbon deposition on the catalyst surface is very limited!!!

only ca. 0.3 wt.% to the catalyst mass after 24 hours of TOS in propane DH!

Such low coke formation is a reason of stable work of VO$_x$/Si-support catalysts, which do not possess strong acid-sites.
Conclusions

- Selective reaction pathways in ODH over VO$_x$-species can be controlled by variation of nature of oxidizing agent and their concentration, regulating oxygen species of certain reactivity, selectivity and concentration.

- Non-oxidative alkane dehydrogenation over VO$_x$-species offers an additional very selective pathway of olefins formation. Their relative contribution to the overall olefin production depends on reaction condition (temperature, contact time) and oxygen content in reaction feeds.

- VO$_x$-species can work very selectively in alkanes dehydrogenation reaction. Isobutene selectivity above 80% and CO$_x$ selectivity below 2 % were achieved at isobutane conversions above 50%. In propane dehydrogenation, selectivity to propylene above 80% was achieved at propane conversion above 40%. This appears to be attractive for industrial applications.

- This knowledge in combination with deeper understanding of structural and surface properties of oxide catalysts may be useful for the development of catalytic materials or ways of operation, which can allow the production of olefins with high selectivity at alkane conversions as high as possible and minimized CO$_x$ production.