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Toluene total oxidation over CuO-CeO_2/Al_2O_3 catalyst: nature and role of oxygen species

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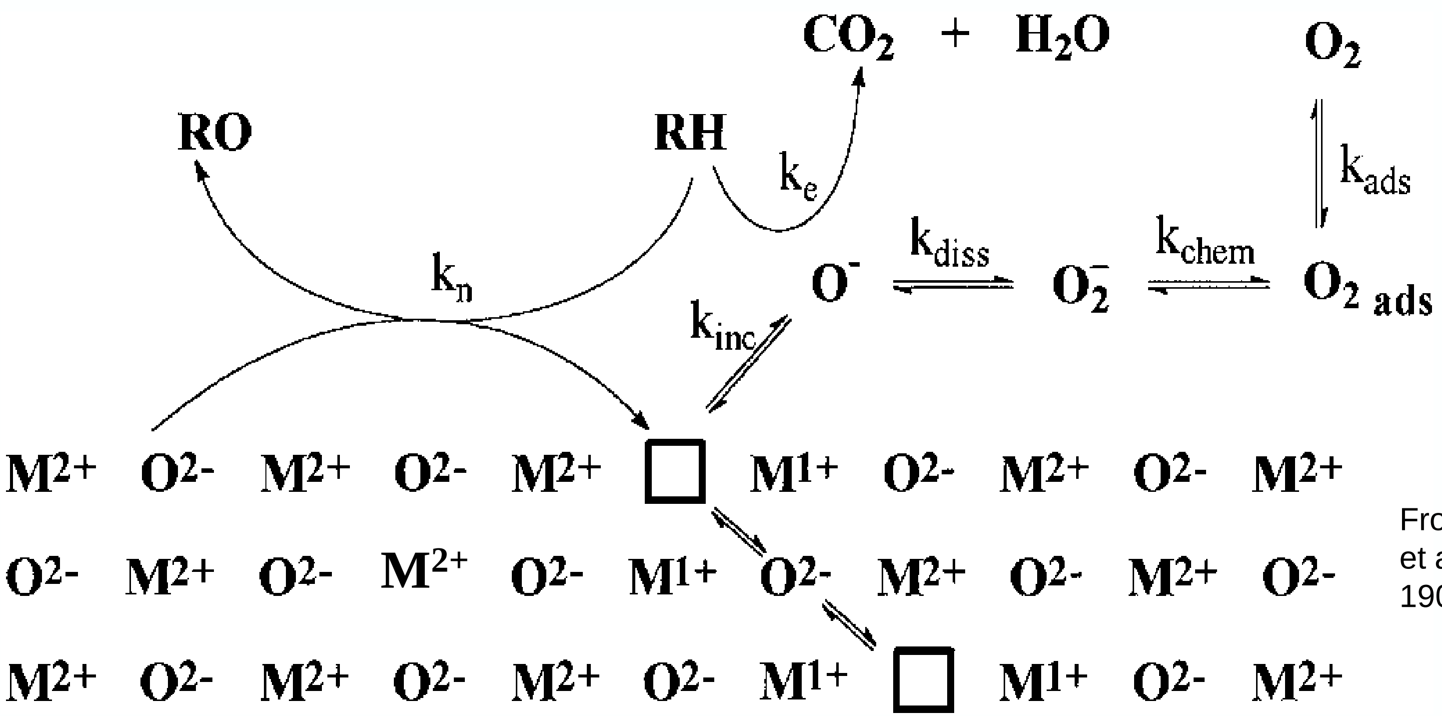
ERIC a.i.s.b.l. European Research Institute of Catalysis

Overview

- Introduction
- Experimental methodology
- Results
- Conclusions

Introduction



From J. Haber et al., J. Catal. 190 (2000) 320

$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$

Catalyst used: (11.6wt.%)CuO-(6.34wt.%)$CeO_2/\gamma\text{-}Al_2O_3$

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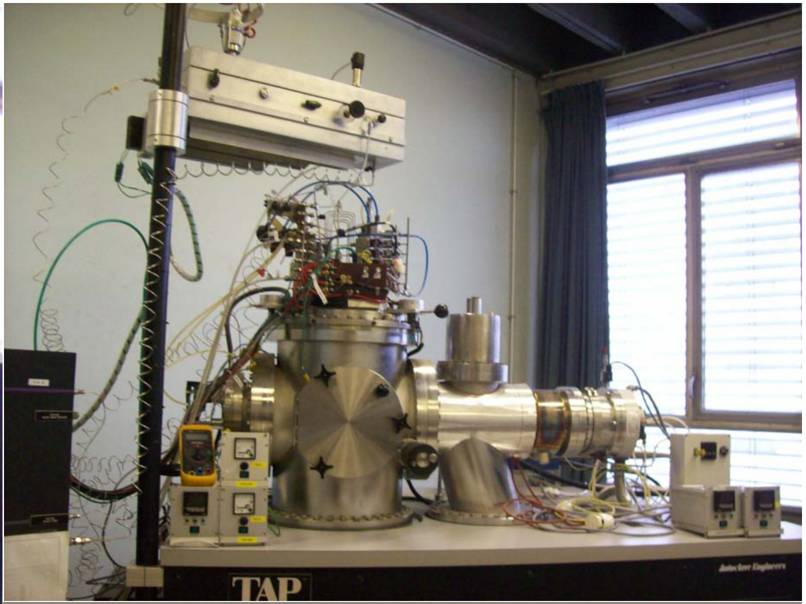
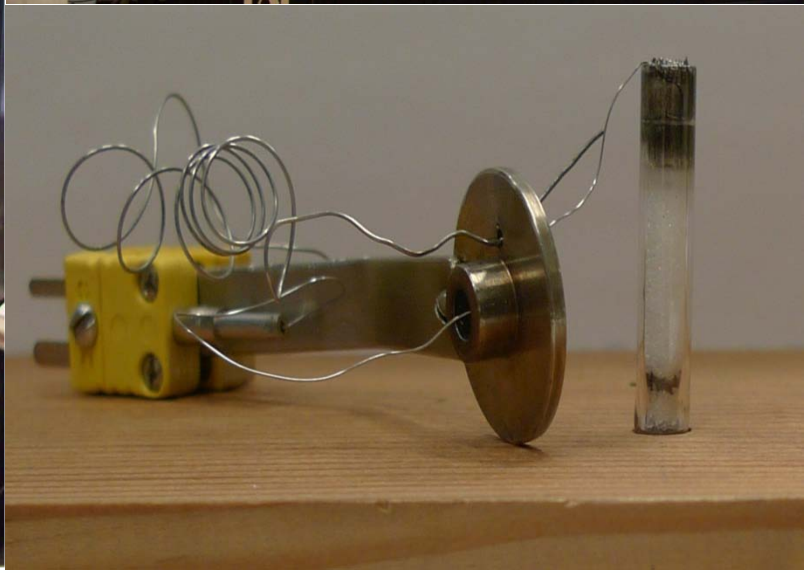
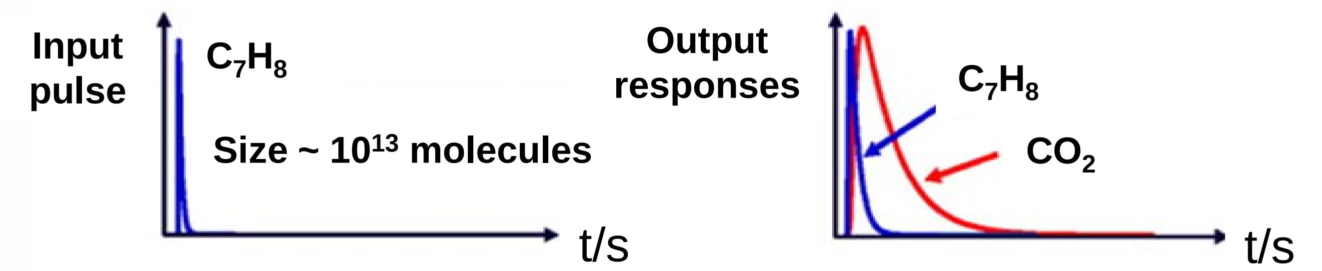
TAP reactor system





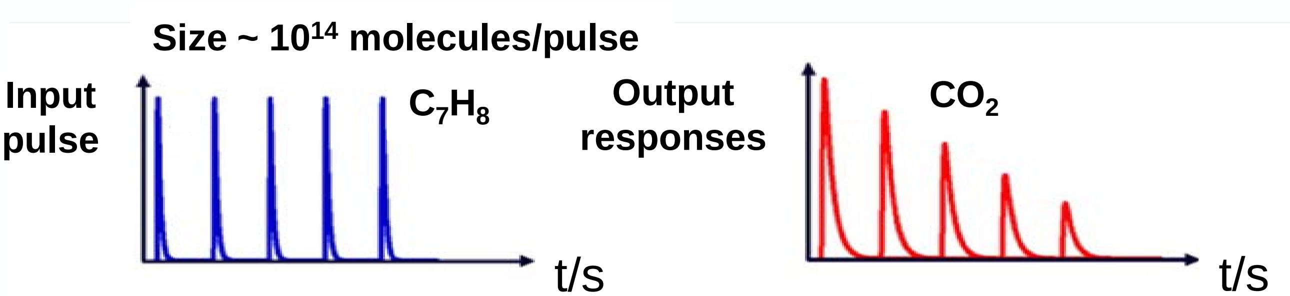
Types of experiments

Single pulse experiment



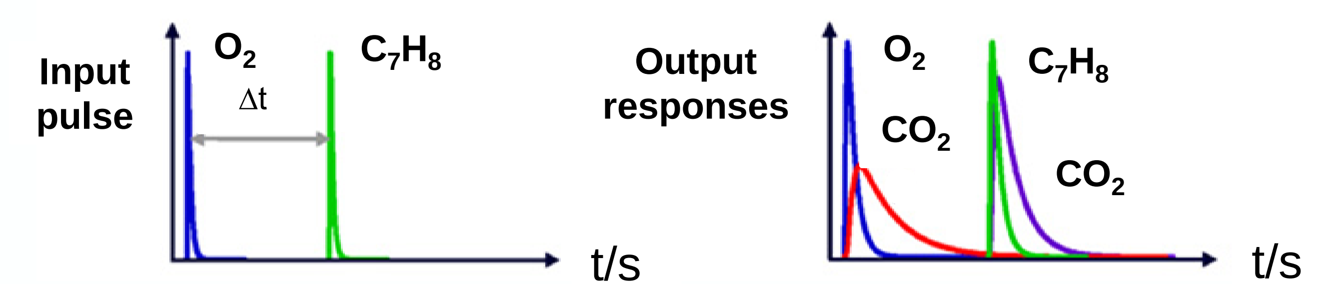
- Knudsen diffusion regime
- No change in the state of the catalyst

Multi pulse experiment



- Molecular diffusion regime
- Deliberate change in the state of the catalyst

Alternating pulse experiment



-Two pulses of different gases
- By varying the time delay of the pulses, lifetime of intermediates can be determined

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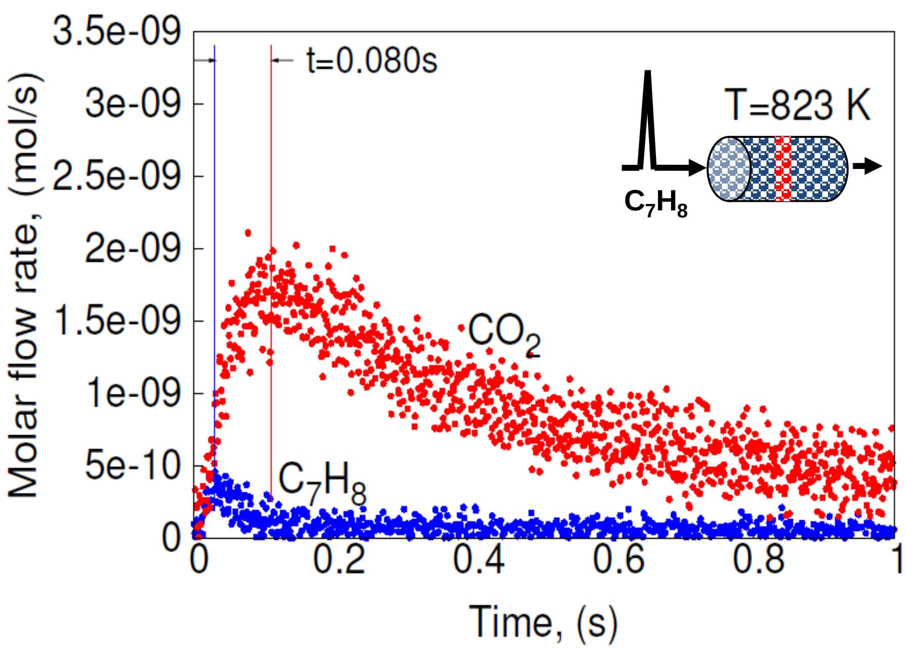
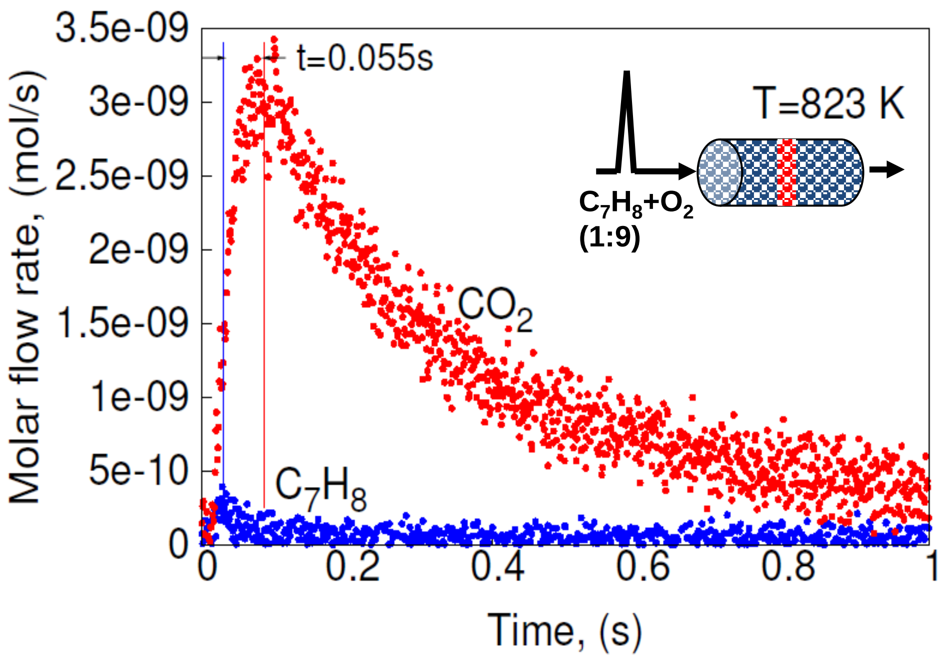
Toluene total oxidation



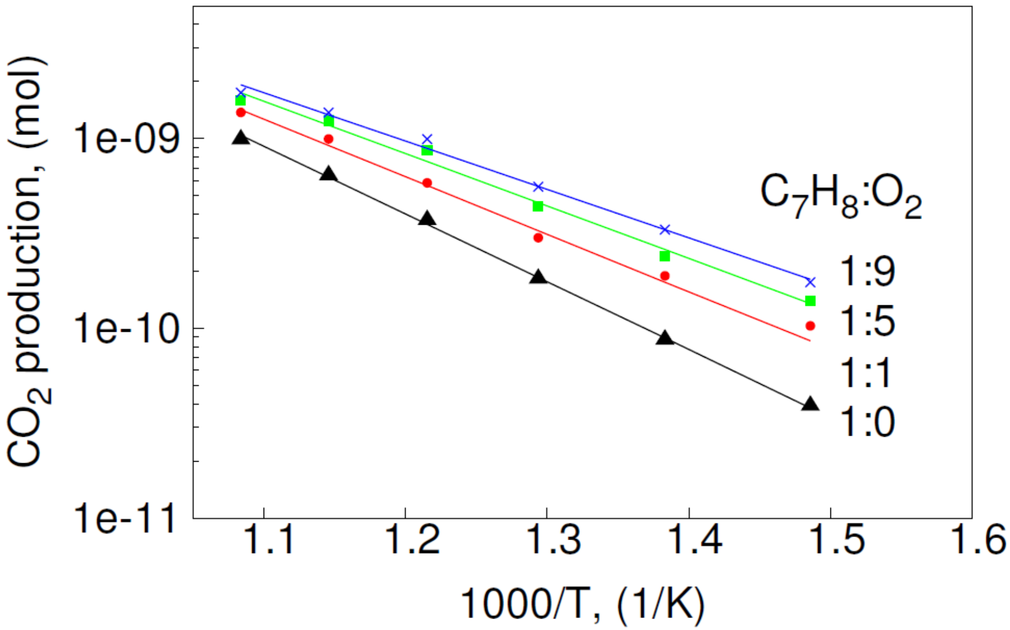
Oxidation of Toluene occurs by Mars and van Krevelen mechanism



Conversion of toluene to CO_2 is more when feed has oxygen

In presence of oxygen the catalyst can be oxidized by lattice and/or surface oxygen species

Effect of partial pressure of di-oxygen



C_7H_8/O_2 ratio	Activation energy (kJ/mol)
1:0	68
1:1	59
1:5	51
1:9	49

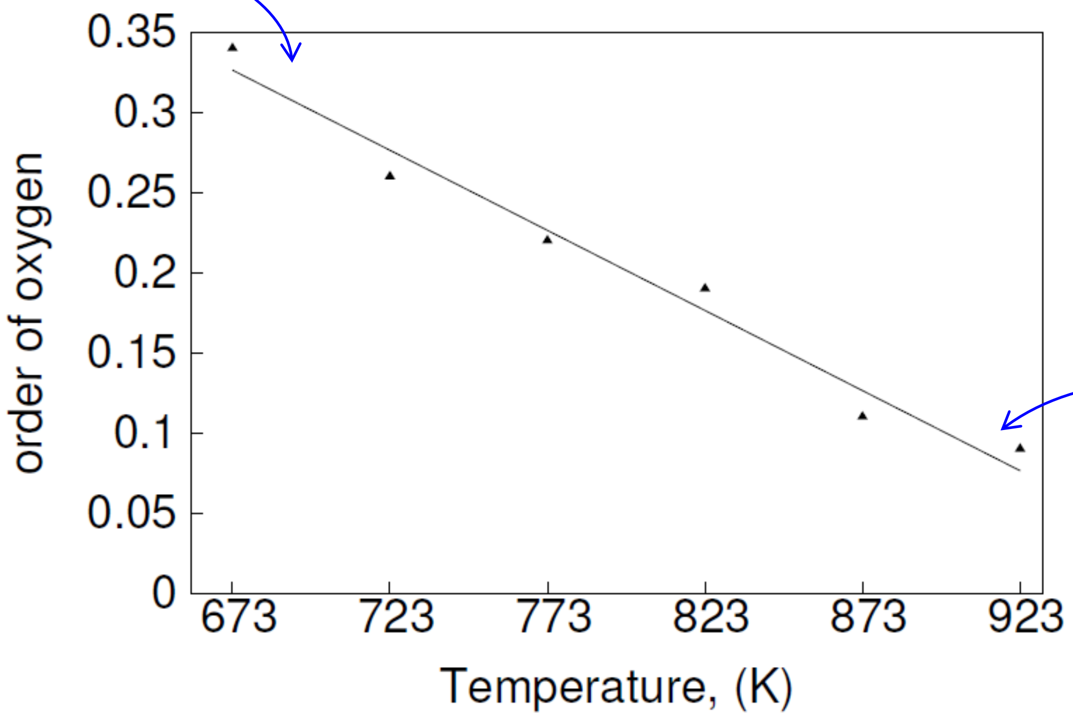
-18 O atoms required for one C_7H_8
-Catalyst reduces with toluene pulse
-Denies easy supply of oxygen
-oxygen has to diffuse from the bulk
-higher activation energy

-Catalyst reduces with toluene pulse
-oxygen supplied from the feed
-lower activation energy
-triggers reaction

Reaction order of di-oxygen

Competition between surface oxygen and lattice oxygen

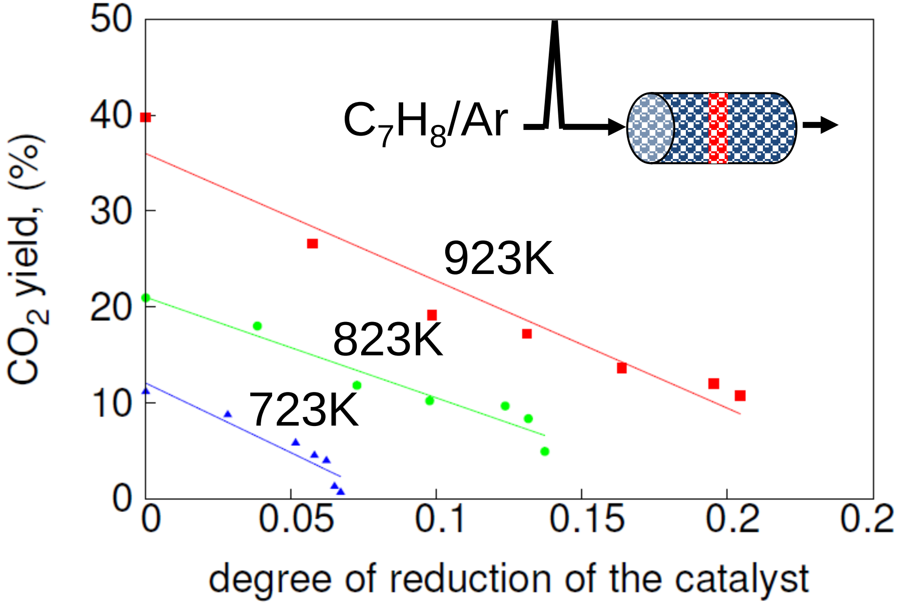
more di-oxygen takes place in reaction



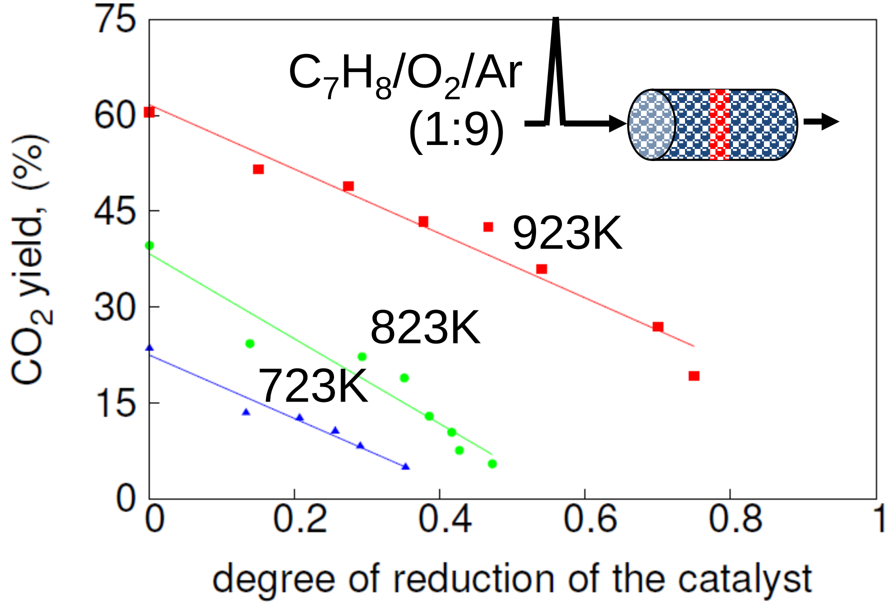
mobility of O atoms in the catalyst is higher, lattice oxygen takes place mainly in reaction

Reaction rate vs. degree of reduction

Catalyst reduced by toluene



Catalyst reduced by CO

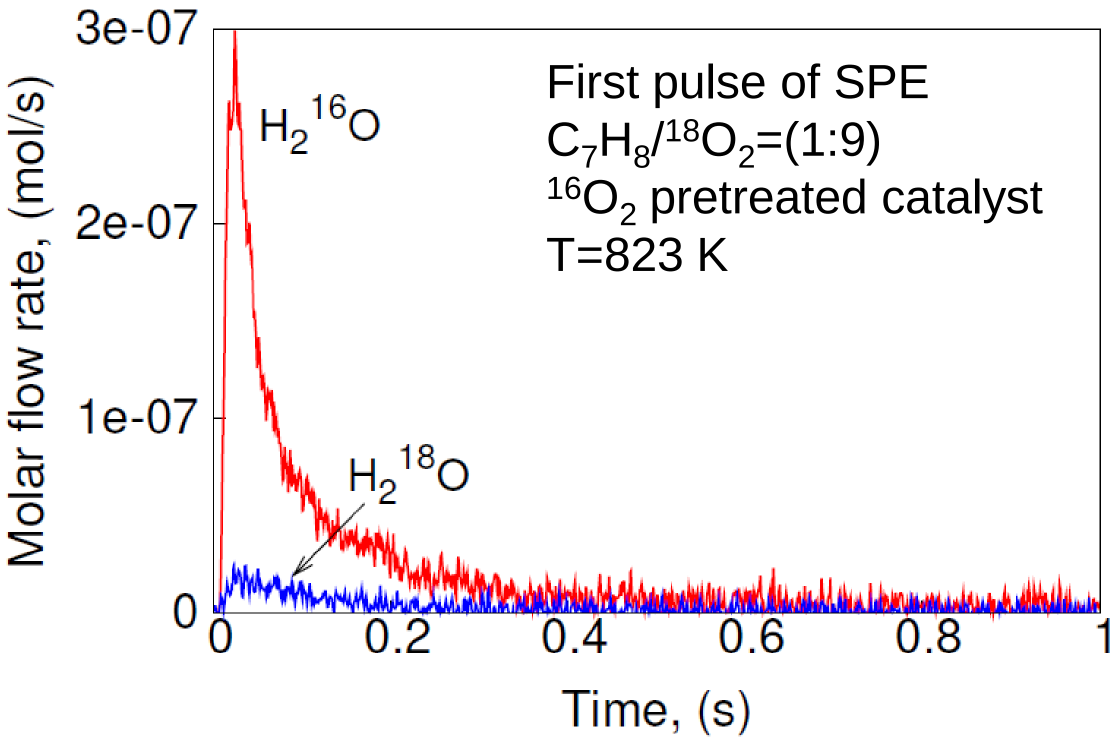


Catalyst cannot be deeply reduced by toluene

In the presence of di-oxygen in the feed, catalyst active at higher degrees of reduction

Reaction is very sensitive to the degree of reduction of the catalyst

Role of adsorbed oxygen species



Only 10% of water formed contained $H_2{}^{18}O$

Mainly lattice oxygen participates in reaction

$C_7H_8 + \chi\,{}^{16}O_L \rightarrow \chi\Box + \chi H_2{}^{16}O + C_7H_{8-2\chi}$

$C_7H_8 + \chi\,{}^{18}O_s \rightarrow \chi H_2{}^{18}O + C_7H_{8-2\chi}$

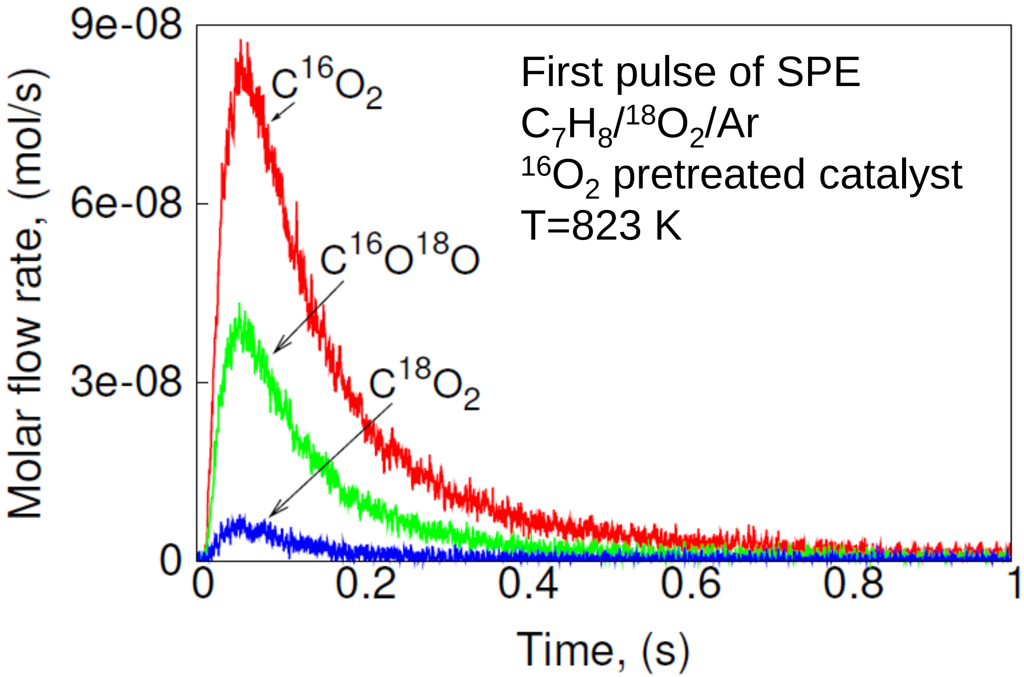
$C_7H_8 + \chi\,{}^{18}O_L \rightarrow \chi\Box + \chi H_2{}^{18}O + C_7H_{8-2\chi}$

$\Box + {}^{18}O_2 \leftrightarrow {}^{18}O_L + {}^{18}O_s$

${}^{18}O_s + \Box \leftrightarrow {}^{18}O_L$

$\Box + {}^{16}O_L{}^{b} \leftrightarrow {}^{16}O_L + \Box_{b}$

Role of adsorbed oxygen species



^{18}O starts occupying the vacant lattice sites

^{18}O in CO_2 is significantly higher than that in water

- **Reaction occurs through Mars and van Krevelen mechanism.**
- **O_2 is mainly required for reoxidation of the reduced surface metal centers.**
- **Separation of contribution of surface oxygen species is not elucidated.**

$C_7H_{8-2\chi} + (18-\chi)^{16}O_L \rightarrow (18-\chi)\square + 7C^{16}O_2 + (4-\chi)H_2{}^{16}O$

$C_7H_{8-2\chi} + (18-\chi)^{18}O_L \rightarrow (18-\chi)\square + 7C^{18}O_2 + (4-\chi)H_2{}^{18}O$

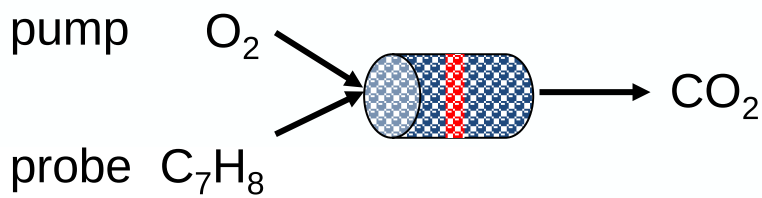
$C_7H_{8-2\chi} + (18-\chi)^{18}O_s \rightarrow 7C^{18}O_2 + (4-\chi)H_2{}^{18}O$

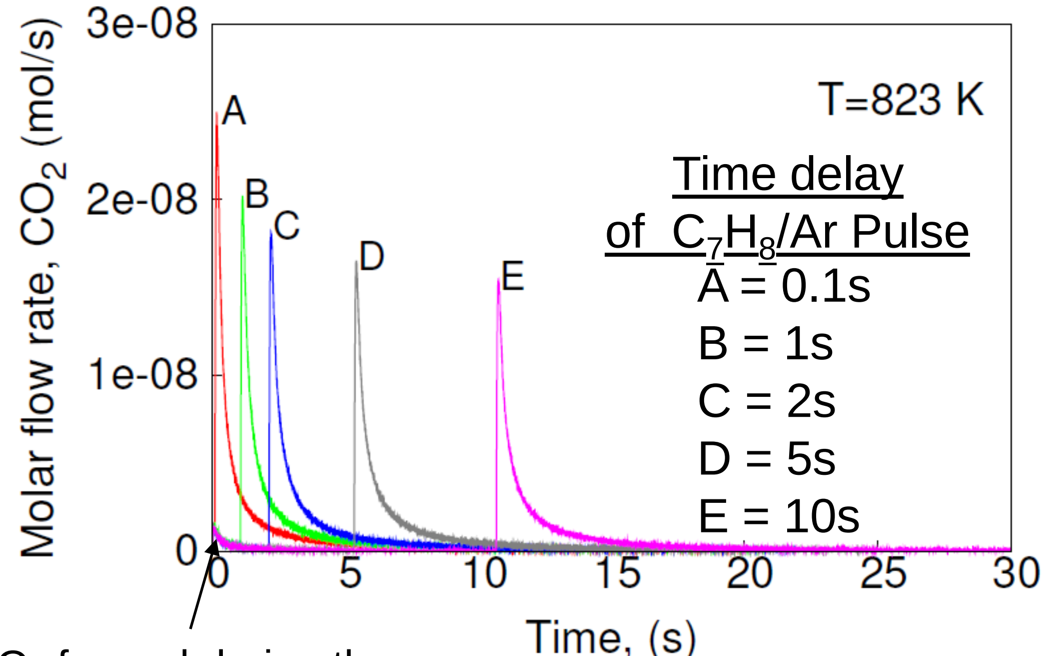
$C_7H_{8-2\chi} + (9-\chi/2)^{16}O_L + (9-\chi/2)^{18}O_L \rightarrow (18-\chi)\square + 7C^{16}O^{18}O + (2-\chi/2)H_2{}^{16}O + (2-\chi/2)H_2{}^{18}O$

$C_7H_{8-2\chi} + (9-\chi/2)^{16}O_L + (9-\chi/2)^{18}O_s \rightarrow (9-\chi/2)\square + 7C^{16}O^{18}O + (2-\chi/2)H_2{}^{16}O + (2-\chi/2)H_2{}^{18}O$

Life time of active surface oxygen

Alternating Pulse experiment





CO_2 formed during the O_2 pulse – constant amount at all time delays of toluene

-Time delay between toluene and oxygen pulse was kept constant

-Time delay between oxygen and toluene pulse was varied

-CO_2 response collected during the C_7H_8 pulse varied in size until time delay of C_7H_8 pulse =5s

Lifetime of active surface oxygen species ~ 1s

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Conclusions

1. Total oxidation of toluene is carried out by the redox, Mars-van Krevelen mechanism.

2. Toluene total oxidation is very sensitive to the degree of reduction of the catalyst.

3. The activity of the copper oxide catalyst in the presence of gas phase oxygen is determined by weakly bound oxygen forms. Life time of this oxygen under reaction conditions is close to 1s.

4. Oxygen isotope exchange experiment shows that surface oxygen could participate in the reaction.

Acknowledgements

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Thank you for your attention !