FACULTY OF ENGINEERING

Analysis of Elementary Surface Reactions in Aromatic Hydrogenation on Pt Using Single-Event MicroKinetics

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Aromatic compounds are **harmful** and easily lead to **uncomplete combustion** of fuels. This results in **soot formation** and the **emission of volatile organic compounds**. These issues can be addressed by **aromatic hydrogenation**. This particularly enhances the **quality of the diesel fraction**.

		EU 2000	EU 2005	EU 2009
gasoline	sulphur	150 ppm	50 ppm	10 ppm
	total aromatics	42%	35%	35%
	benzene	1%	1%	1%
diesel	sulphur	350 ppm	50 ppm	50 ppm
	polyaromatic hydrocarbons	11% max	11% max	11% max

A fundamental understanding of the hydrogenation reaction mechanism on a noble metal (Pt) is aimed at. To this purpose a **single-event microkinetic model** is constructed based on previously acquired **experimental data**[1] and on the results of an assessment of the reaction path through **quantum chemical calculations**[2]

Horiuti-Polanyi mechanism:

$H_2(g) + 2* \rightleftharpoons 2H*$ K_{H2}

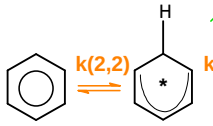
$A(g) + * \rightleftharpoons A*$ K_A

$AH_i* + H* \rightleftharpoons AH_{i+1}* + *$ K_{i+1} (i=0,..5)

$AH_6* \rightleftharpoons AH_6(g) + *$ K_{AH6}

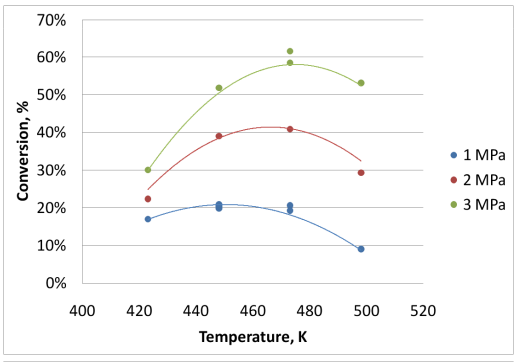
adsorption steps quasi-equilibrated

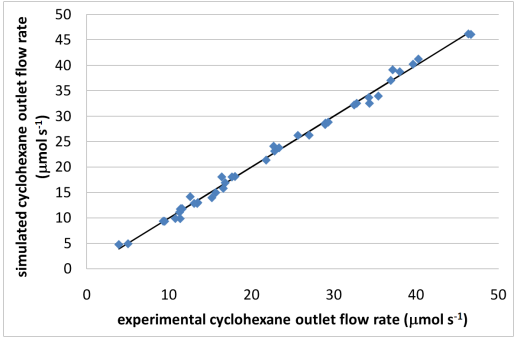
activation energy assessment through ab initio calculations

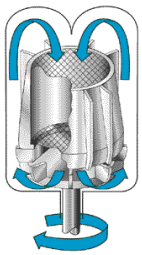


The **Single-Event MicroKinetic** (SEMK) model for aromatic hydrogenation has six reactions families, of which three occur in the reaction network for benzene. The distinctive features are:

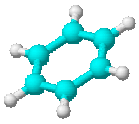
- the **saturation degree** of the nearest neighbour carbon atoms
- the **branching degree** of the hydrogenated carbon atom





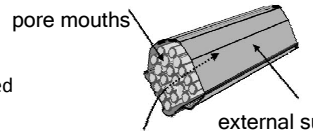


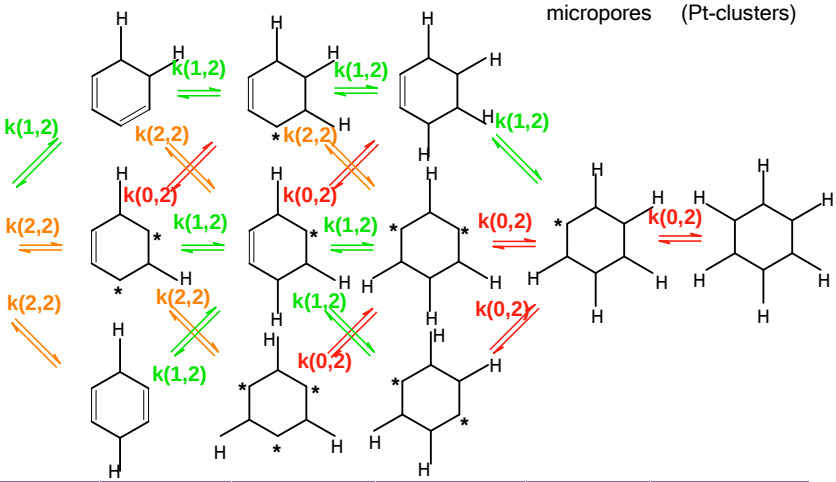
Benzene hydrogenation experiments have been performed in a Berty type reactor on Pt/H-ZSM22. Temperatures ranged from 423 to 498 K, the total pressure from 1 to 3 MPa, the benzene partial pressure from 10 to 60 kPa and that of H_2 from 100 to 600 kPa. The space time is varied up to 100 kg_{cat} s mol^{-1}.



Benzene was selected as model component because of the **few possible secondary acid catalyzed reactions** that is possible

Pt/H-ZSM22 was selected as catalyst as it is expected to limit secondary acid catalyzed reactions by its **shape selective** properties

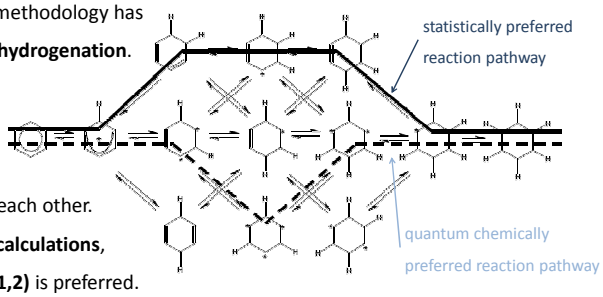




	separate E_a	separateE_a $E_a(1,2)$ higher	$E_a(0,2)$ = $E_a(2,2)$	$E_a(0,2)$ = $E_a(2,2)$ $E_a(1,2)$ higher	identical E_a	quantum chemistry
$E_a(0,2)$	61,9 ± 2,1	48,1 ± 3,8	62,2 ± 0,6	57,7 ± 0,5	58,7 ± 0,5	ΔE_a = 71,0 ± 0,03
$E_a(1,2)$	50,9 ± 15,3	66,0 ± 1,0	49,8 ± 0,8	65,0 ± 1,7	58,7 ± 0,5	-
$E_a(2,2)$	66,5 ± 0,6	61,0 ± 0,5	62,2 ± 0,6	57,7 ± 0,5	58,7 ± 0,5	-
$\Delta H(0,2)$	2,2 ± 1,3	11,7 ± 2,1	3,2 ± 0,4	7,8 ± 0,4	7,7 ± 0,5	-
$\Delta H(2,2)$	6,5 ± 0,5	0,006 ± 26	3,7 ± 0,4	1,1 ± 0,3	0,7 ± 0,4	-
ΔH_{benz}	-64,5 ± 0,02	-58,3 ± 1,8	-59,8 ± 0,1	-56,0 ± 0,1	-56,1 ± 0,01	-71,0
ΔH_{H2}	-59,6 ± 0,05	-56,2 ± 2,1	-58,8 ± 0,1	-59,4 ± 0,1	-59,4 ± 0,01	-98,5 ± 0,001
# param	7	7	6	6	5	2
RSSQ	28,7	32,6	34,2	40,1	77,8	250
F value	4763	4251	4849	4150	2594	1443

conclusions

The **Single-Event MicroKinetic** (SEMK) methodology has been succesfully extended to **aromatic hydrogenation**. Various scenarios for the considered activation energies lead to rather similar results. On a **statistical** basis **$E_a(0,2)$ and $E_a(2,2)$ can be put equal** to each other. In accordance with **quantum chemical calculations**, the scenario with a **higher value for $E_a(1,2)$** is preferred.



acknowledgements

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[1] Thybaut J.W. et al., Chem Eng. J., 90 (2002) 117. [2] Saeys M. et al, J. Catal., 236 (2005) 129.

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