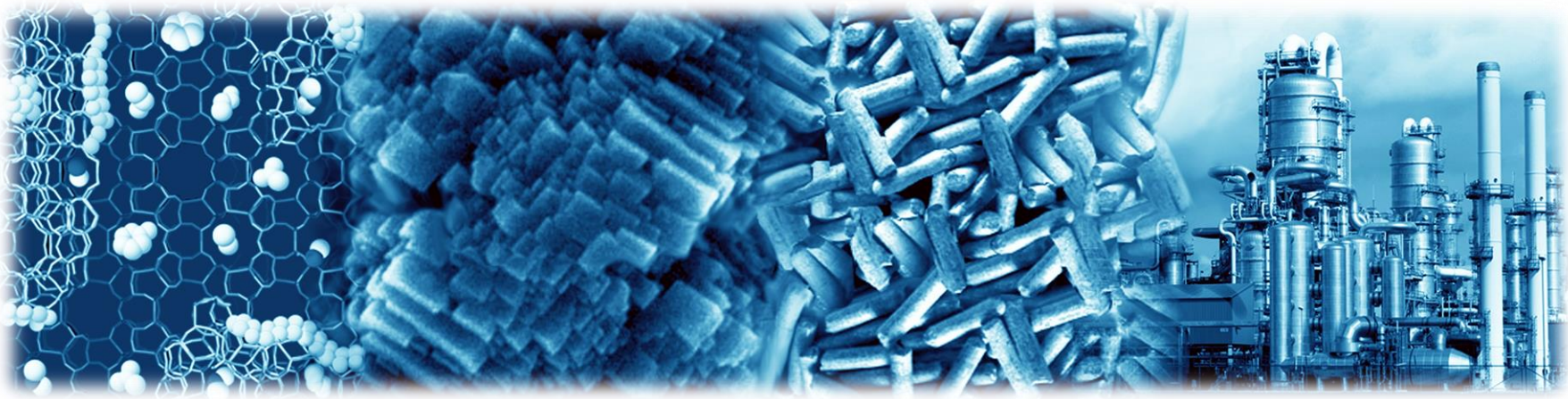
Design of base catalysts for the catalytic deoxygenation of bio-oil by aldol condensation

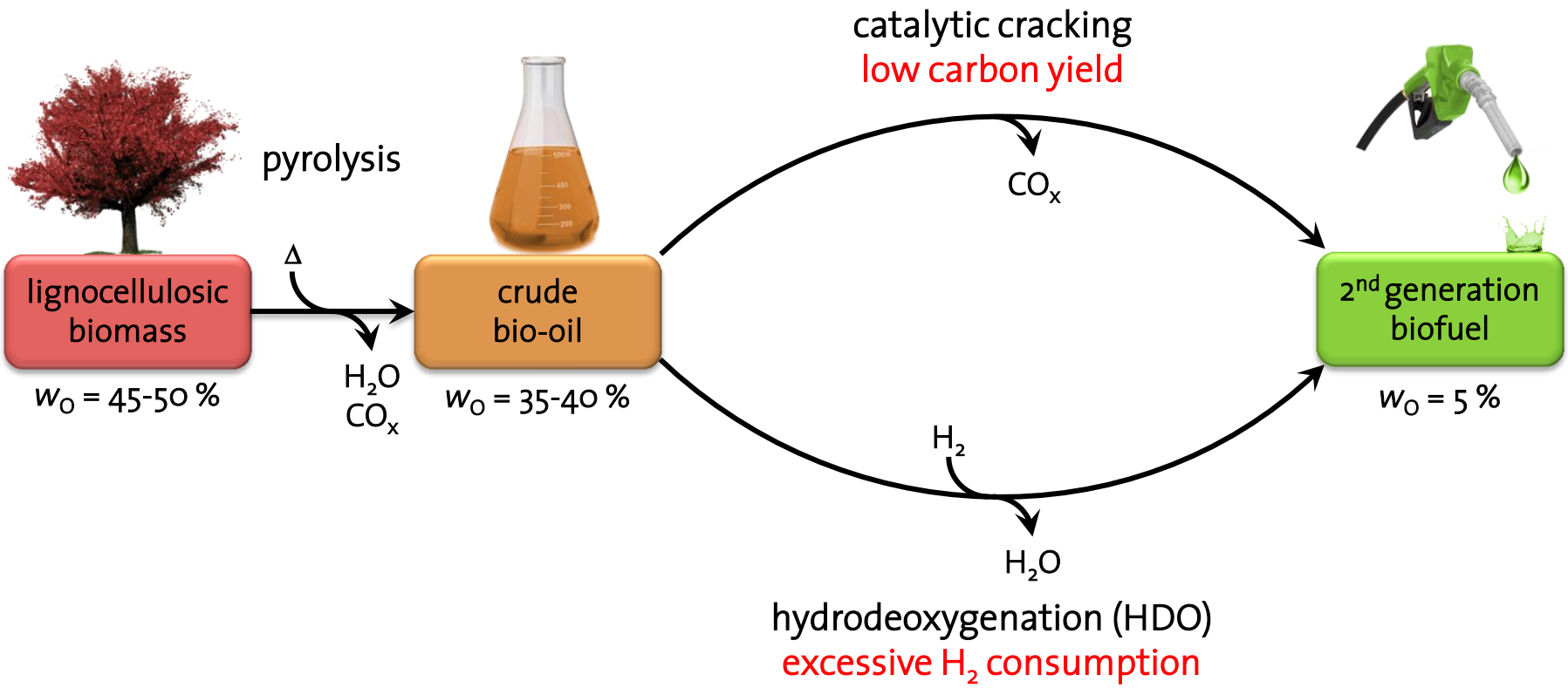


Tobias C. Keller, Begoña Puértolas, Sharon Mitchell, and Javier Pérez-Ramírez

Institute for Chemical and Bioengineering, ETH Zurich, Switzerland

Renewable fuels from biomass feedstocks

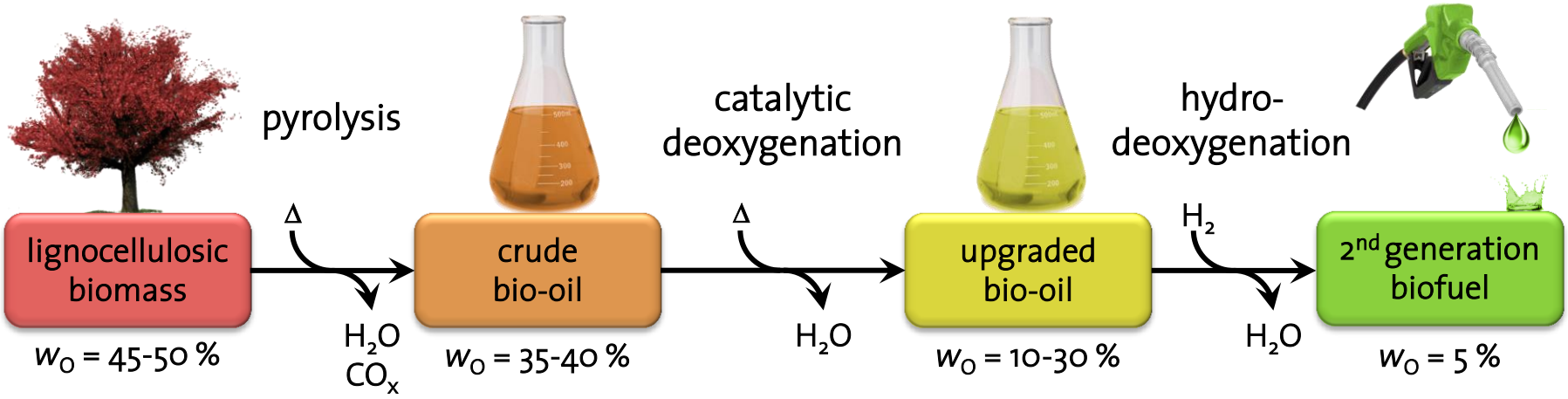
- Deoxygenation of crude bio-oil: Limitations



Renewable fuels from biomass feedstocks

- Cascade deoxygenation of crude bio-oil

cascatbel

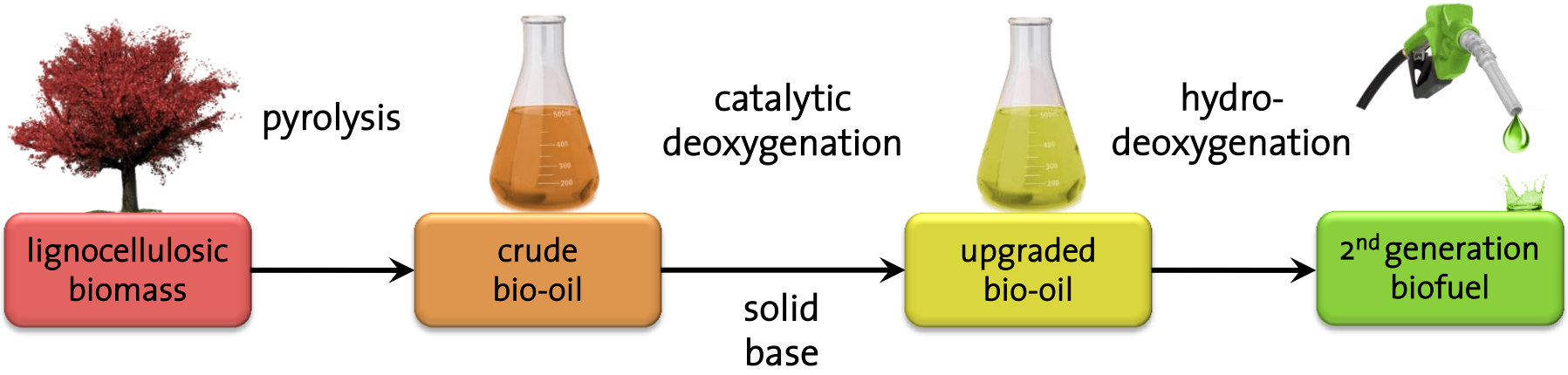


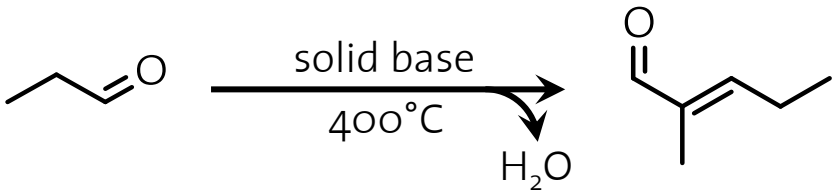
aldol condensation
ketonization
esterification

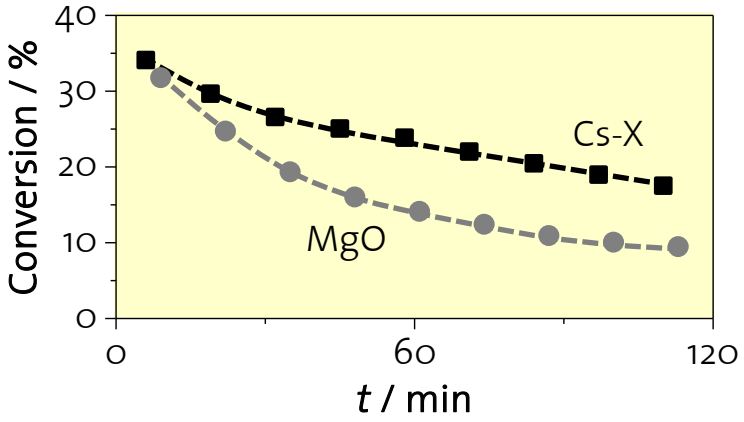
Renewable fuels from biomass feedstocks

- Cascade deoxygenation of crude bio-oil

cascatbel



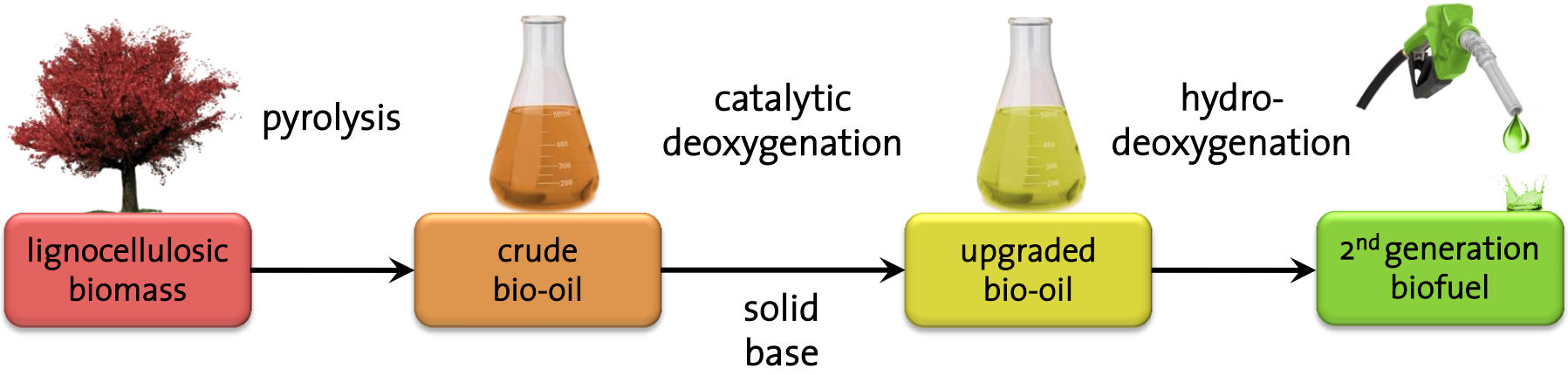




Renewable fuels from biomass feedstocks

- Cascade deoxygenation of crude bio-oil

cascatbel



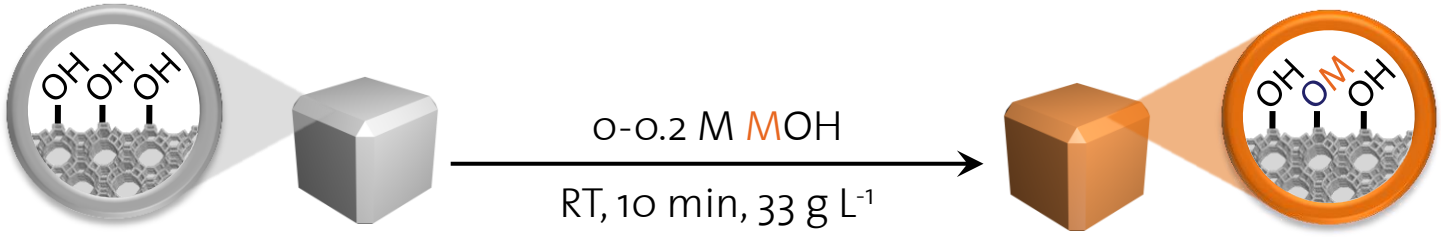
Alkali metal-grafted zeolites

Calcium hydroxyapatites

Mg-loaded zeolites

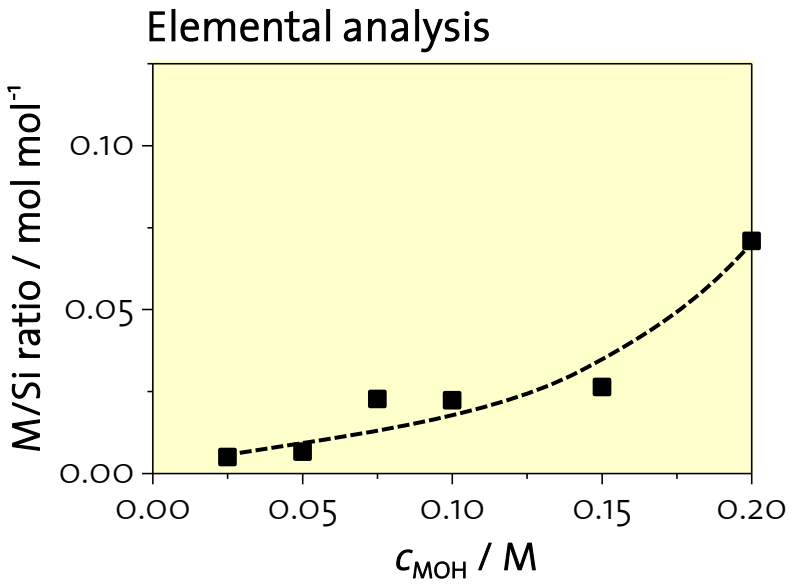
Alkali metal-grafted USY zeolites

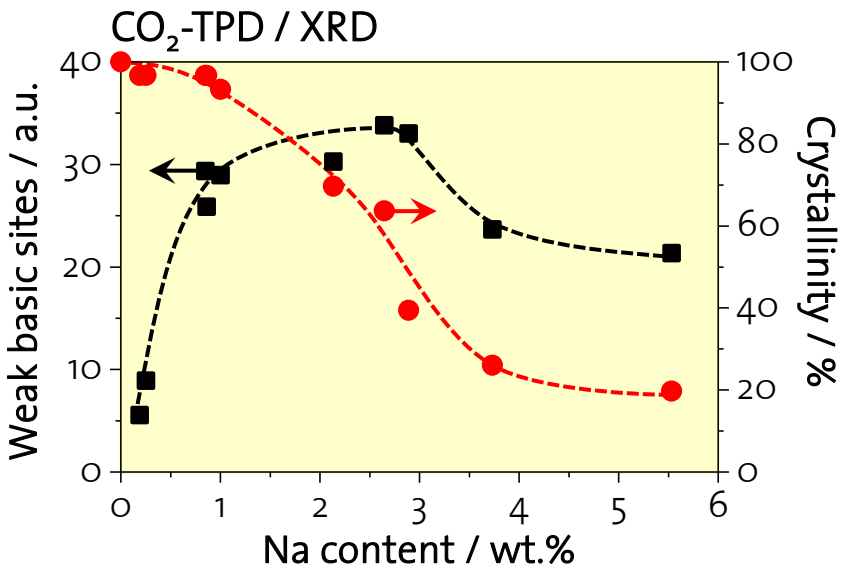
- Generation of basic sites *via* alkaline treatments in alcohols



high-silica USY zeolite

mild base catalyst

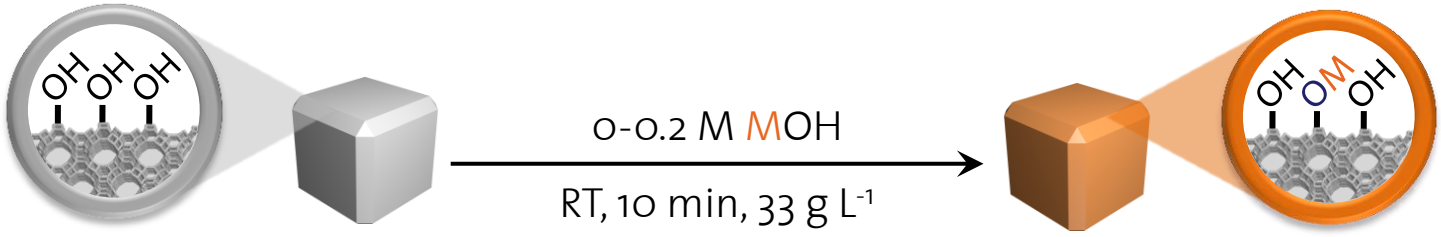




ChemSusChem **2014**, *7*, 1729; ACS Catal. **2015**, *5*, 5388

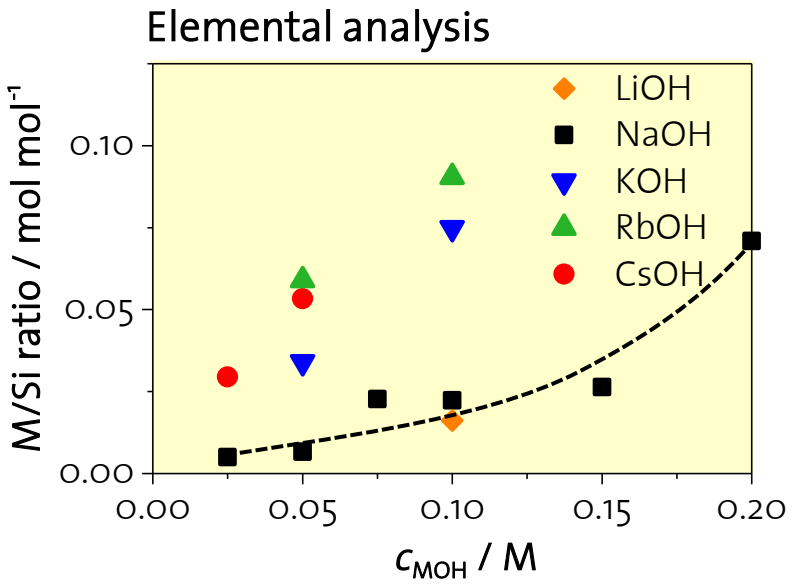
Alkali metal-grafted USY zeolites

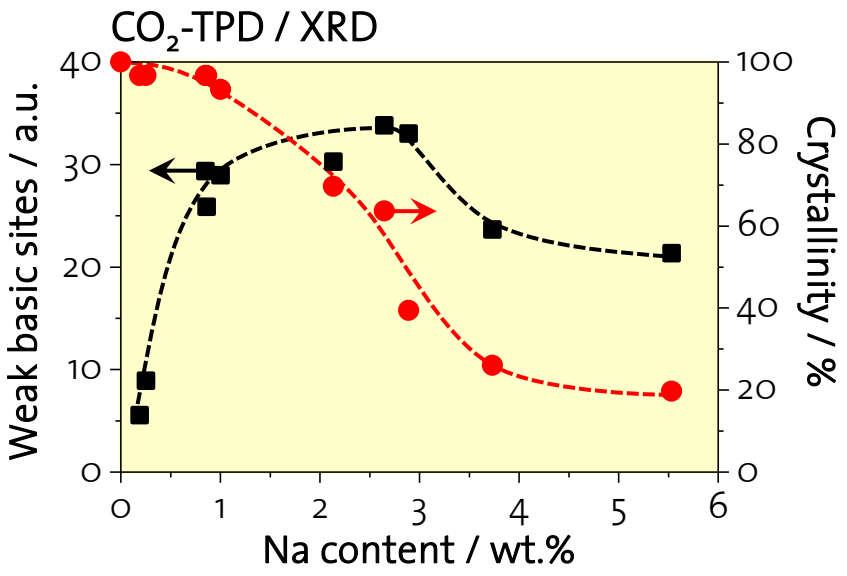
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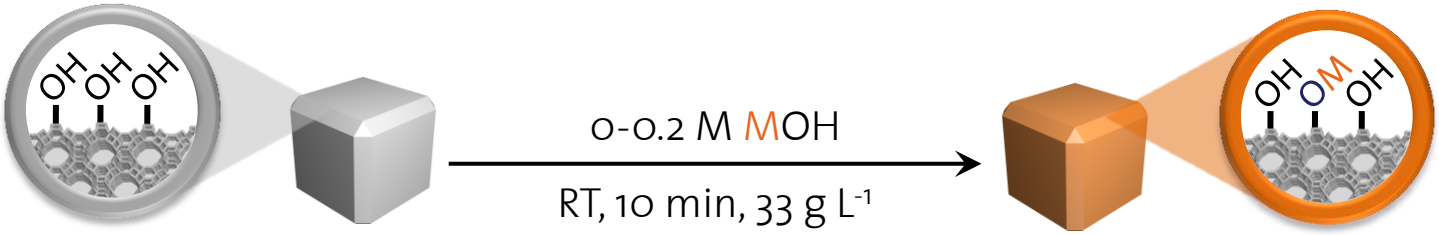




ChemSusChem **2014**, *7*, 1729; ACS Catal. **2015**, *5*, 5388

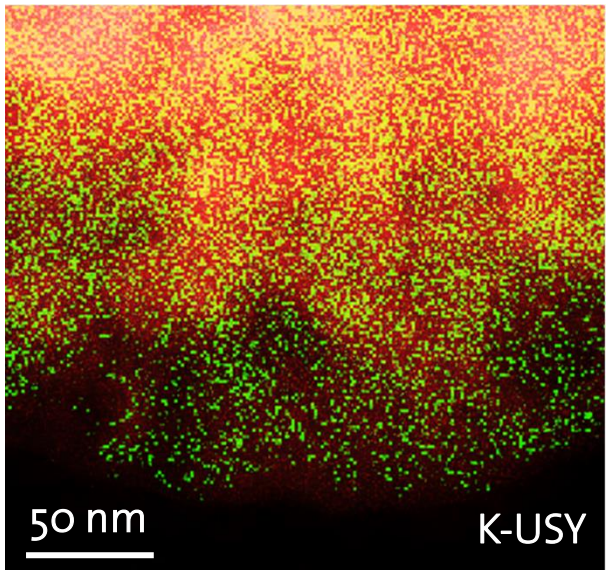
Alkali metal-grafted USY zeolites

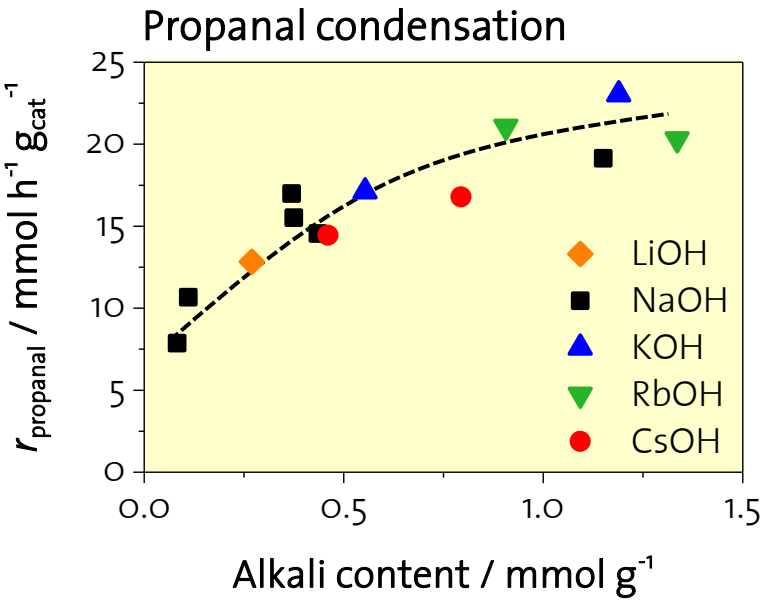
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high-silica USY zeolite

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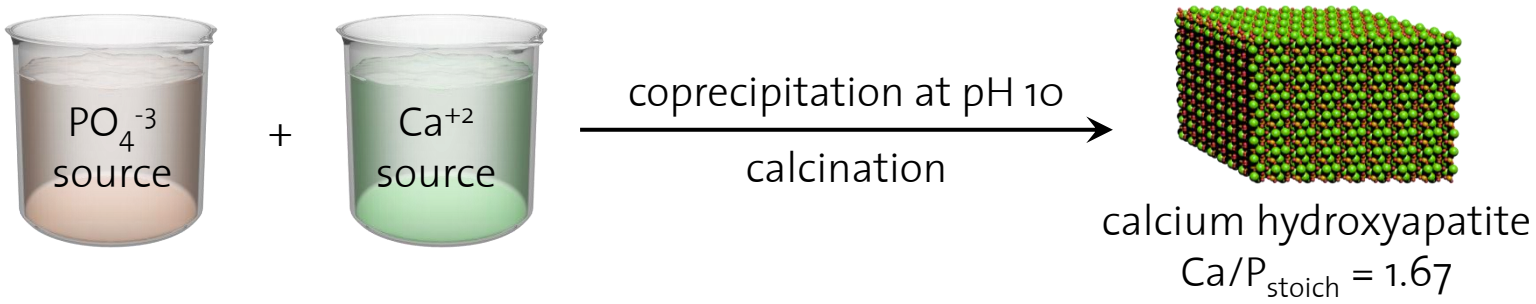


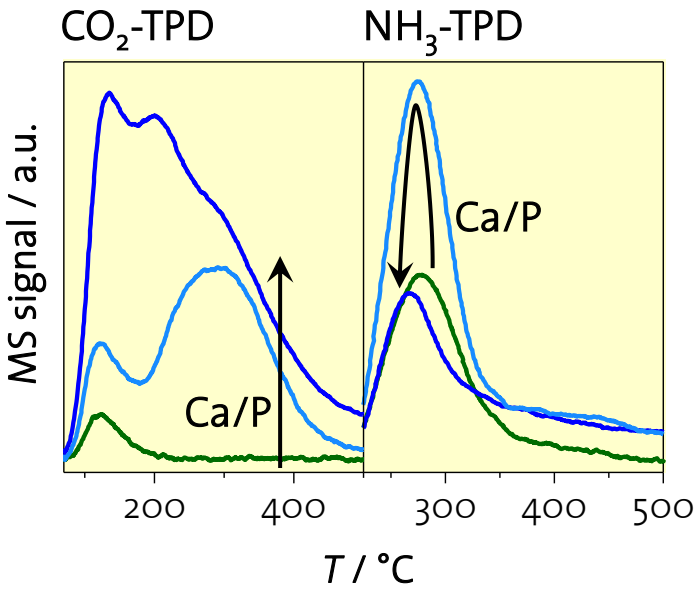


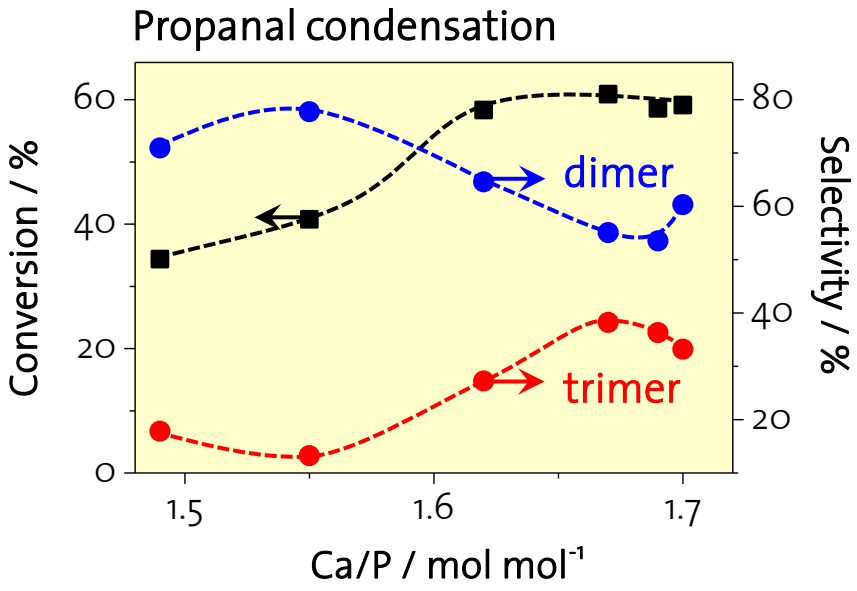
ChemSusChem **2014**, *7*, 1729; ACS Catal. **2015**, *5*, 5388

Calcium hydroxyapatites

- Acid-base bifunctional catalyst



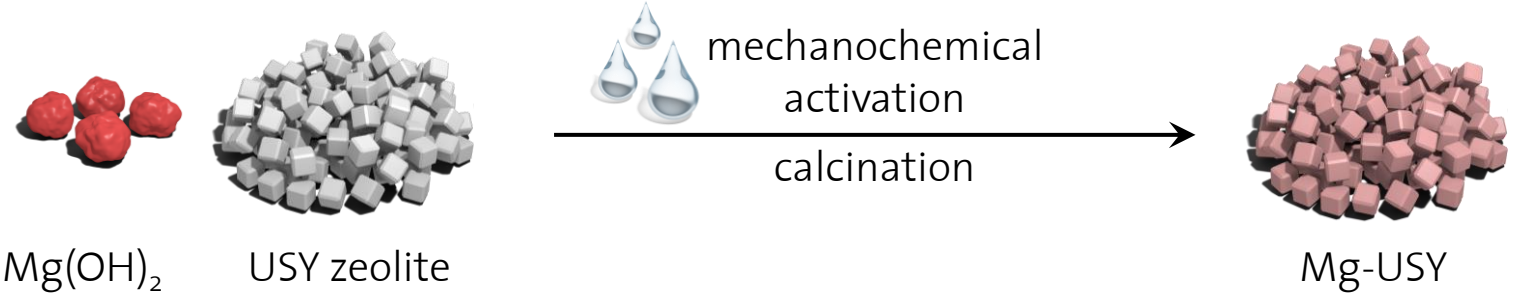


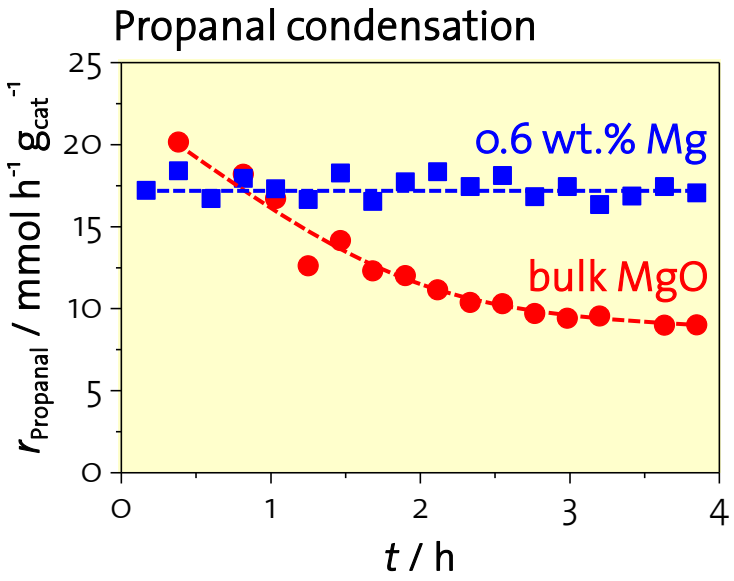


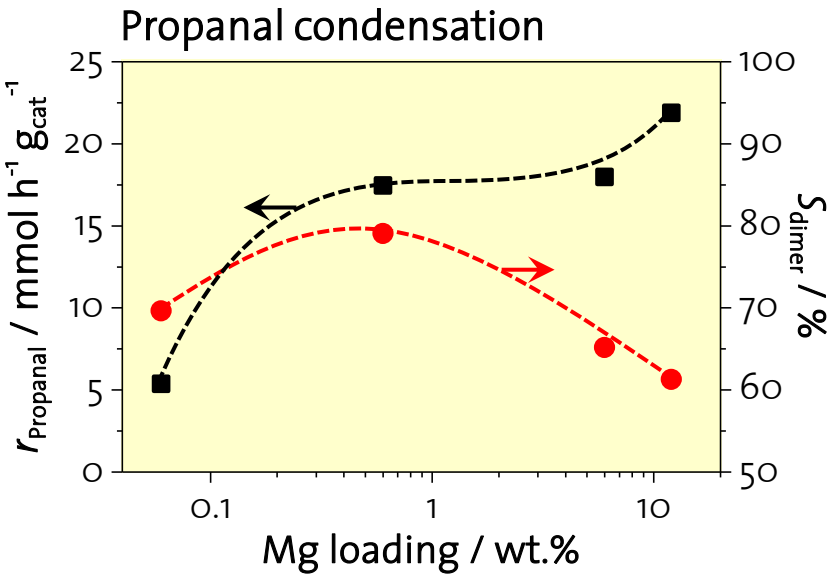
Green Chem. **2014**, *16*, 4870

Mg-loaded USY zeolites

- Moderated basicity through dispersion

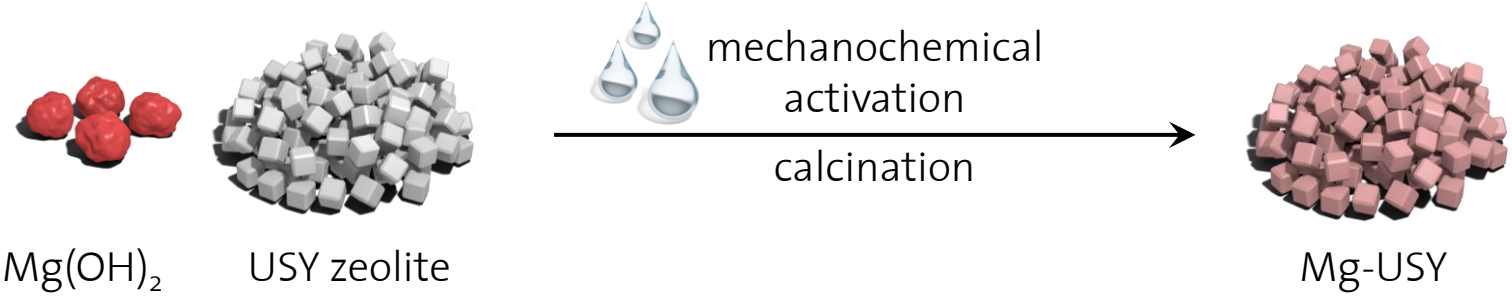


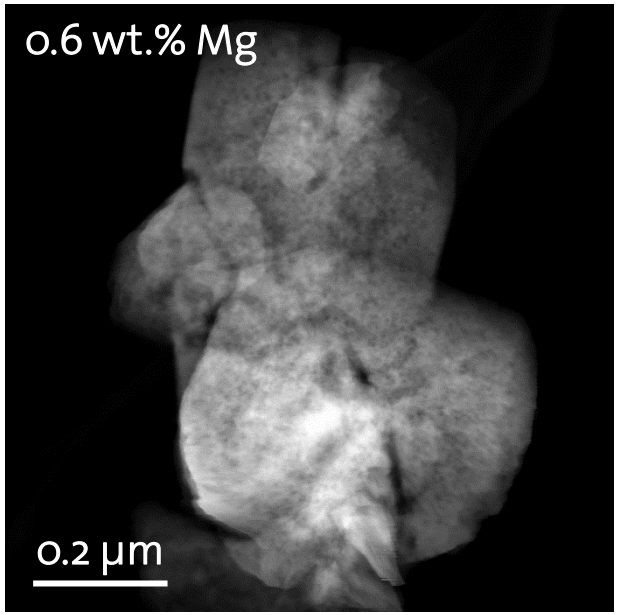


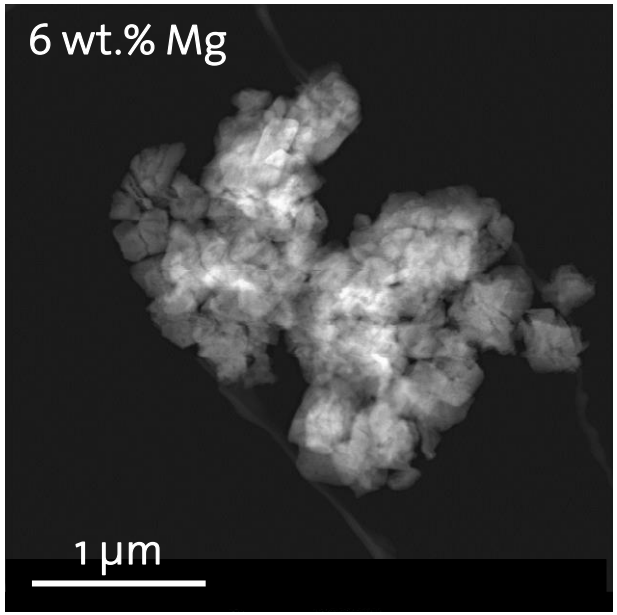


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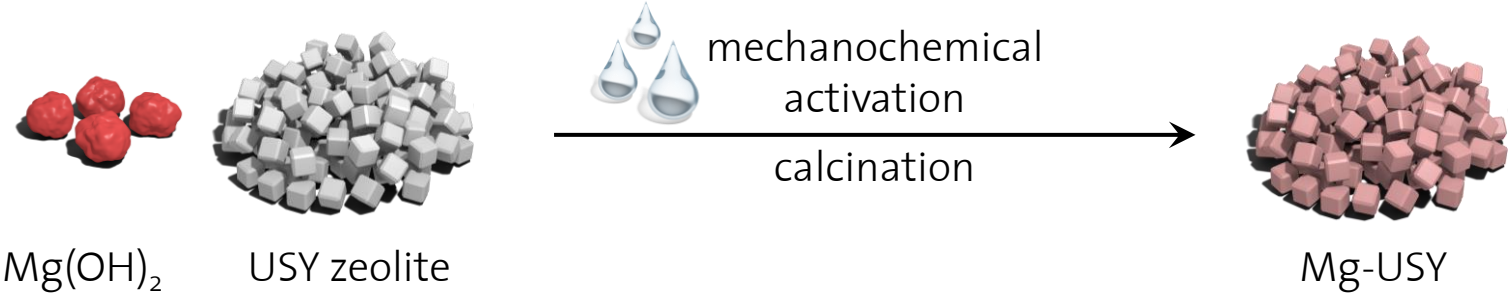


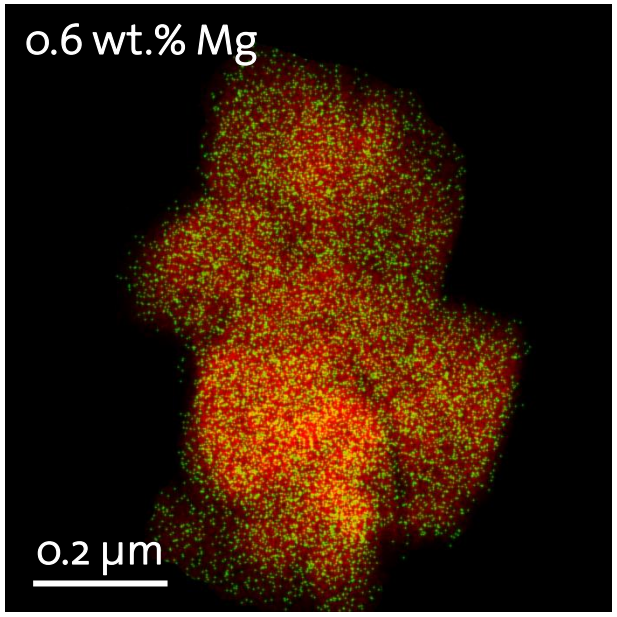


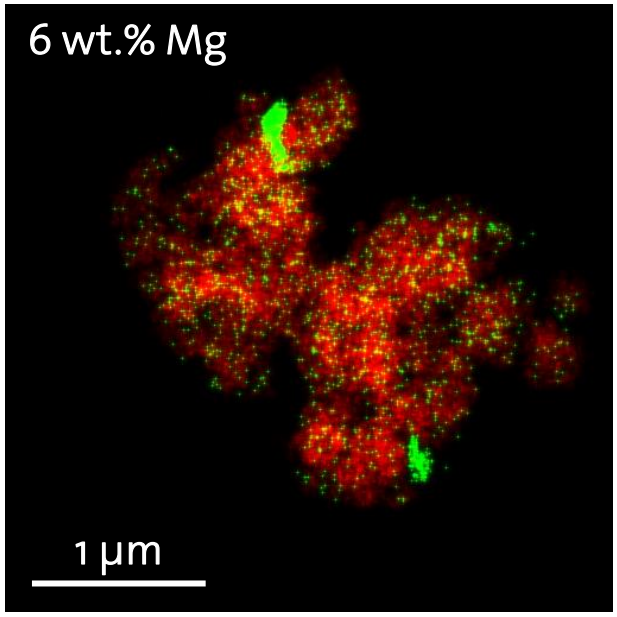


Mg-loaded USY zeolites

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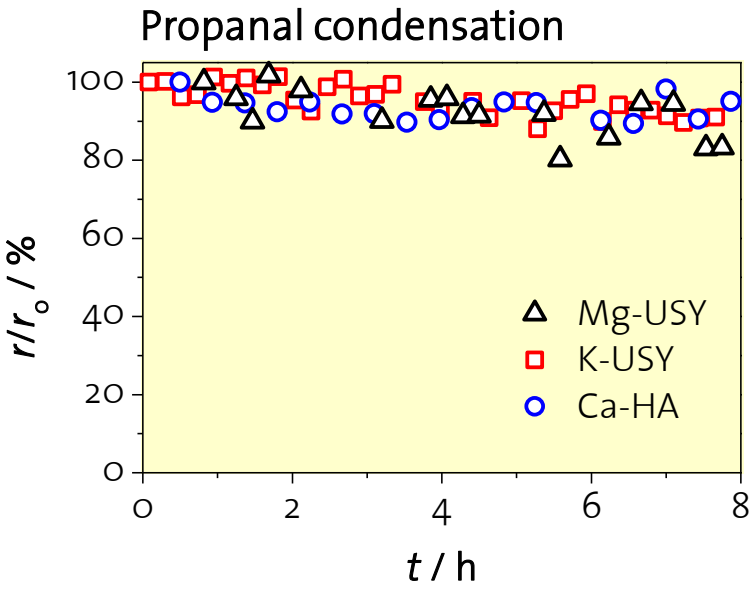






Complexity gap: model compounds and bio-oil

- Stability in the propanal self-condensation

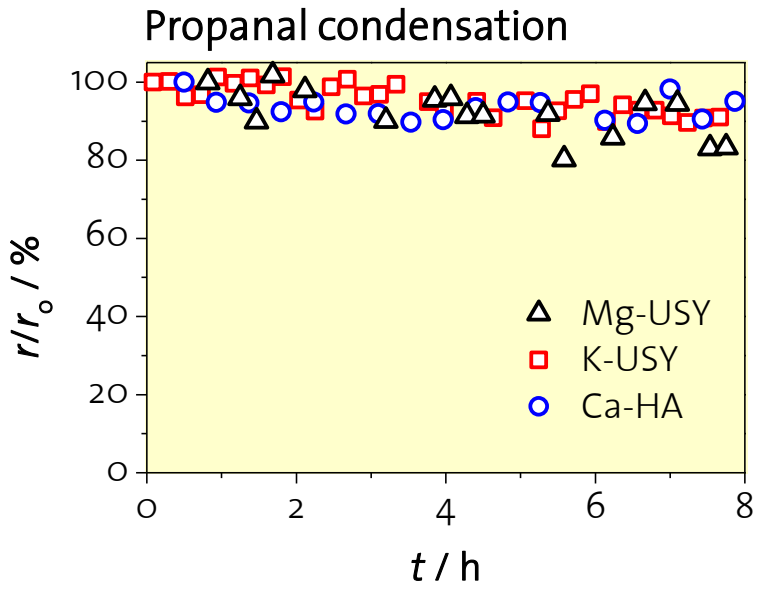




Model compounds

Complexity gap: model compounds and bio-oil

- Stability in the propanal self-condensation



1. Kinetic studies with pure model compounds
2. Binary interaction with representative bio-oil constituents:
   Carboxylic acids, alcohols, and water
3. Model bio-oil feeds



Model compounds

Complexity gap



Bio-oil

Mixtures of propanal with other model compounds

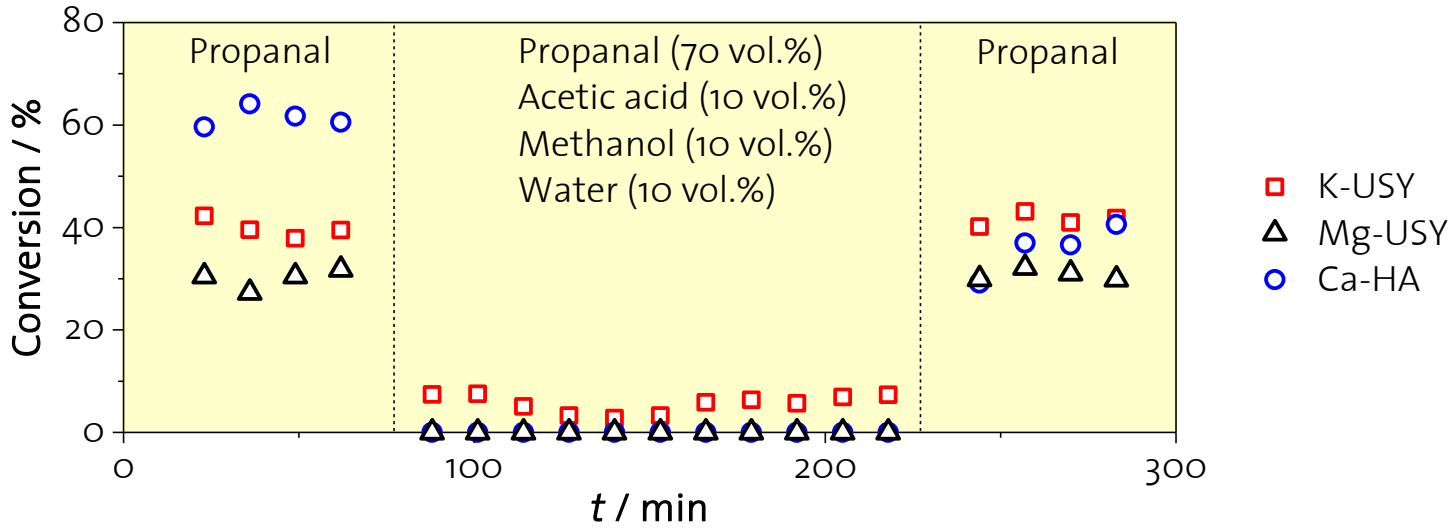
- Reaction orders in binary mixtures with propanal

Reactant	K-USY	Mg-USY	Ca-HA
propanal	1.01	0.72	1.07
acetic acid	-0.40	-0.55	-0.78
methanol	-0.03	-0.06	-0.05
water	-0.05	-0.04	-0.27
surface species	propanal acetic acid	propanal aldol cond. products acetic acid	propanal aldol cond. products acetic acid methanol

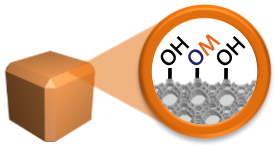
Mixtures of propanal with other model compounds

- Reaction orders in binary mixtures with propanal

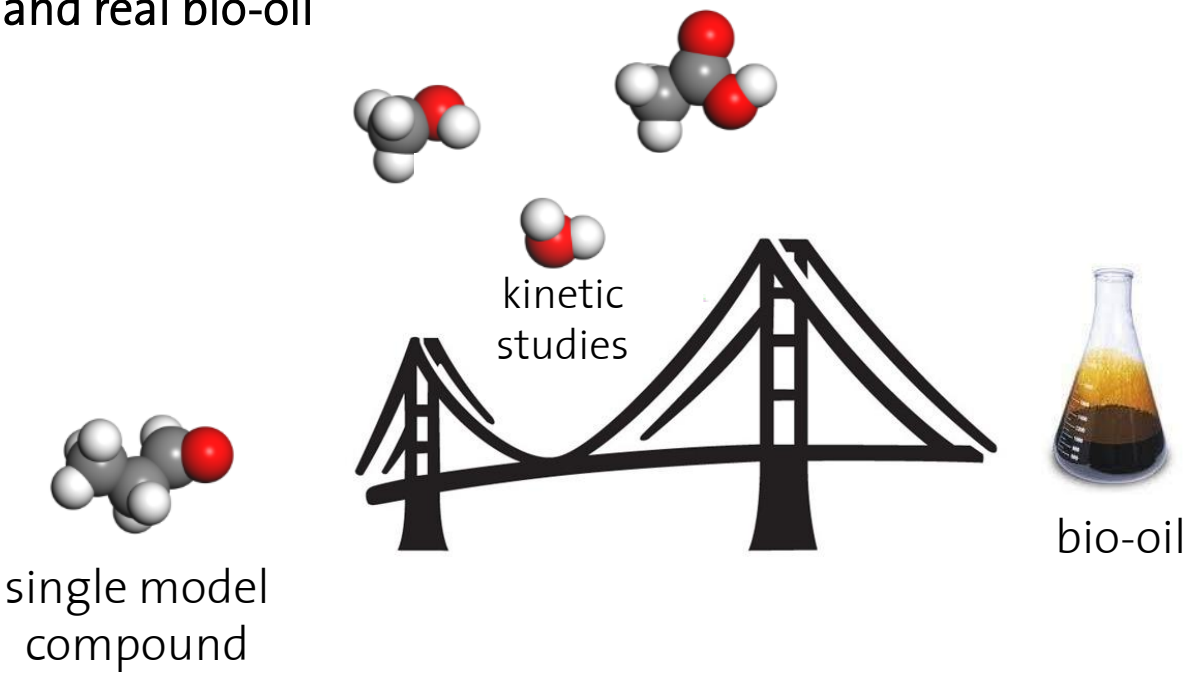
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Conclusions

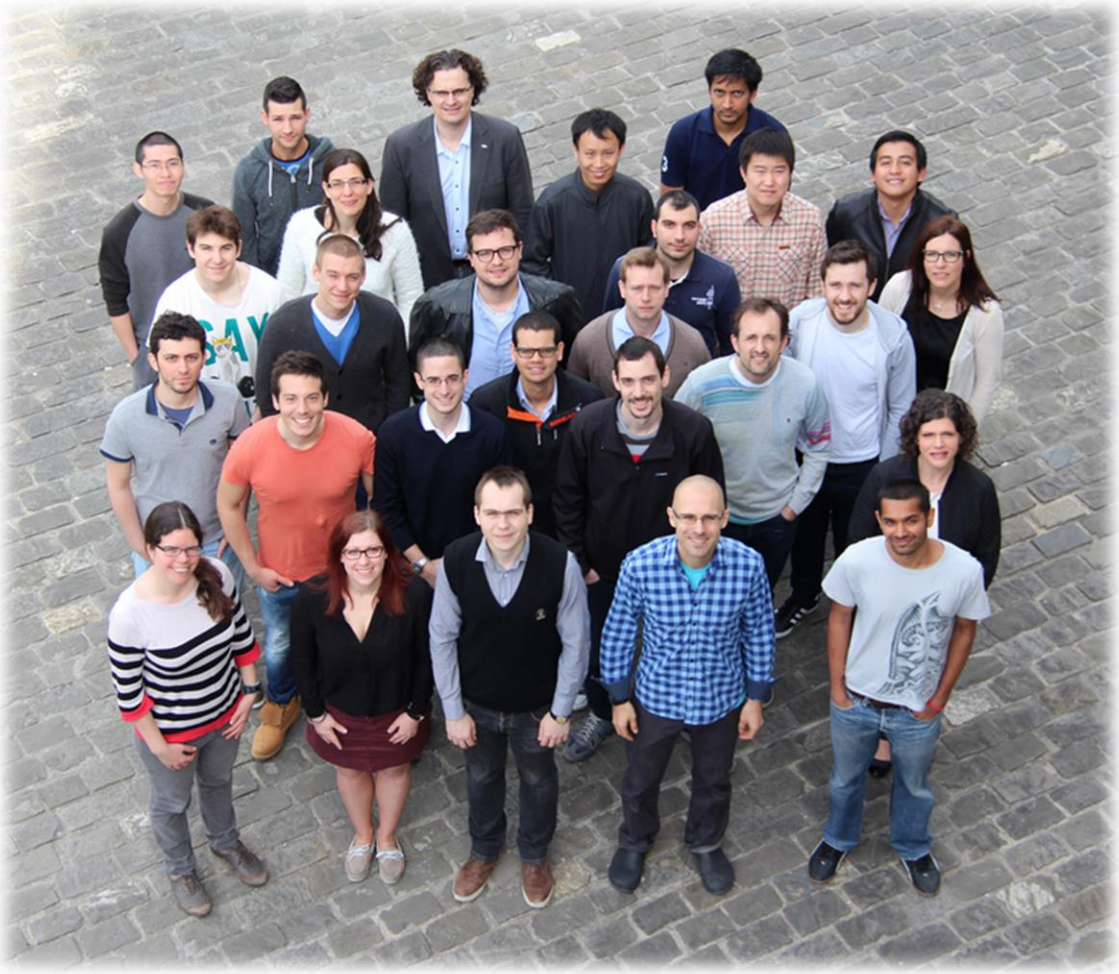


- Mild basic sites are key for high stability and selectivity
- Co-feeding bio-oil constituents as acetic acid strongly impacts on the catalytic performance
- The weak adsorption of substrates on K-USY zeolite makes it resistant to poisoning
- Kinetic studies enable to bridge the complexity gap between model compounds and real bio-oil



Many thanks to...

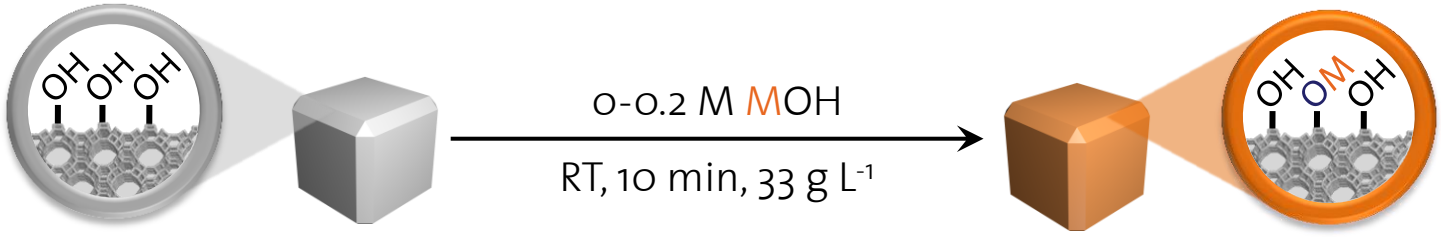
- Kartikeya Desai
- Elodie G. Rodrigues



ETH Research grant
ETH-31 13-1

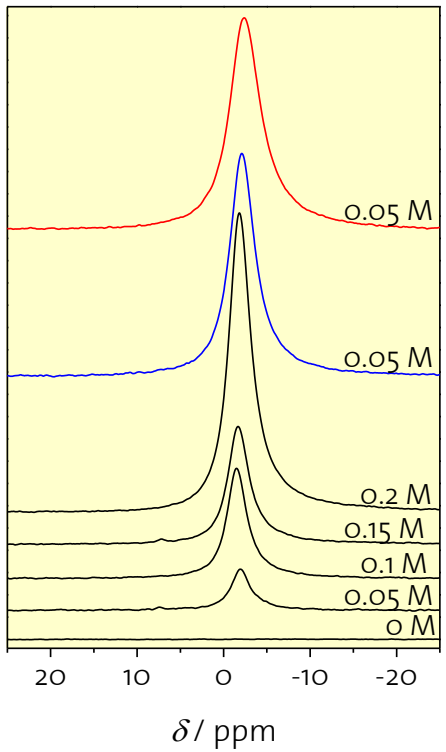
Alkali metal-grafted USY zeolites

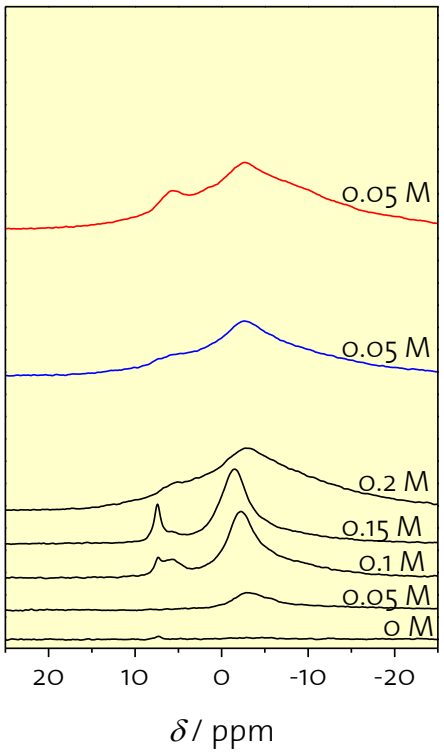
- ^{23}Na MAS NMR

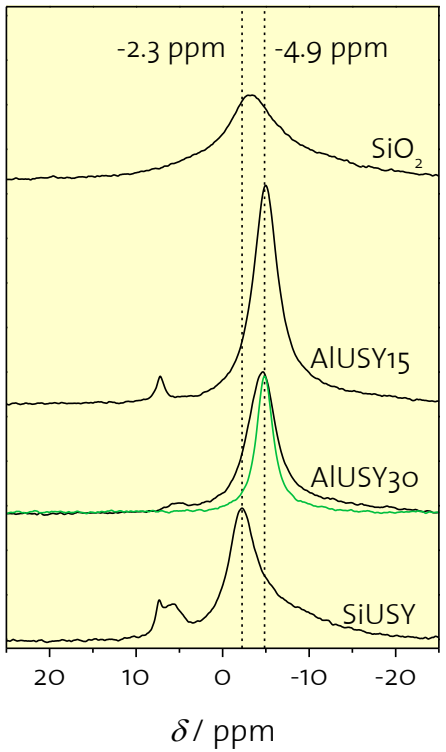


high-silica USY zeolite

mild base catalyst

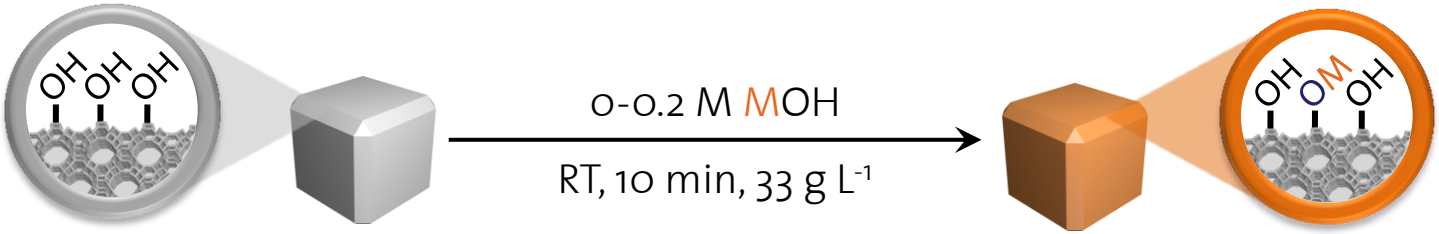






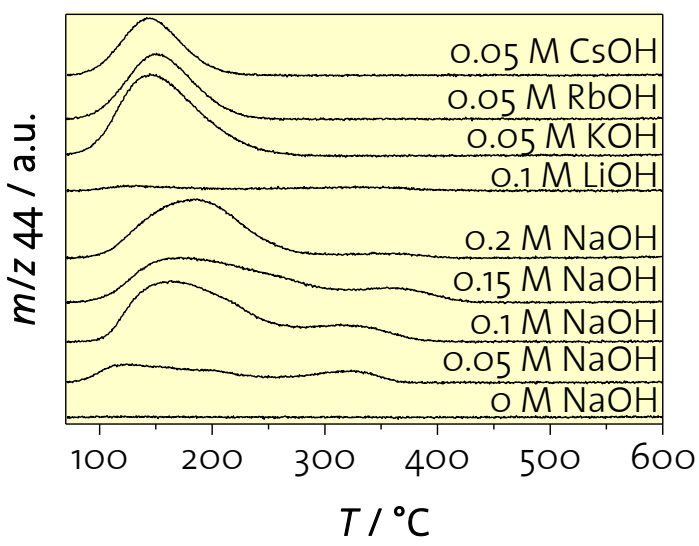
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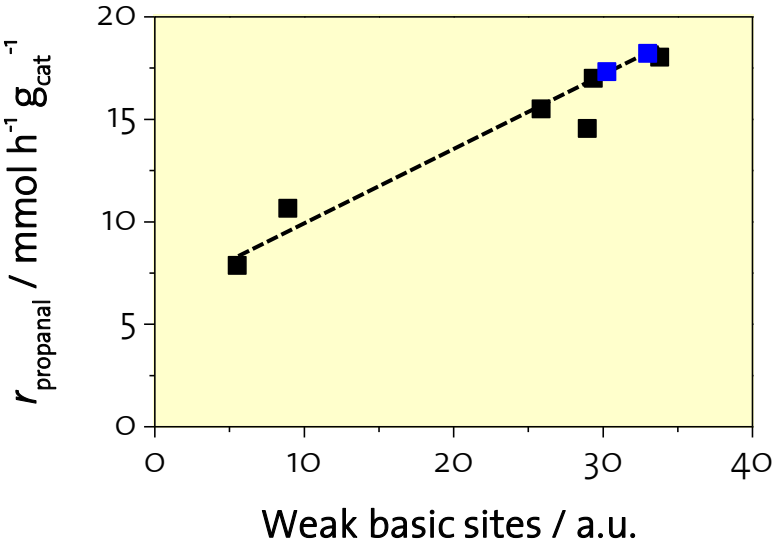
- CO2-TPD profiles



high-silica USY zeolite

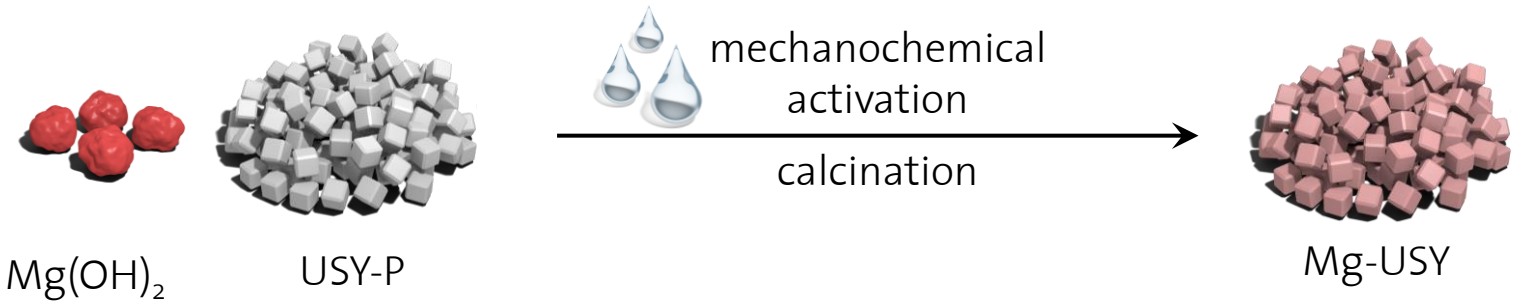
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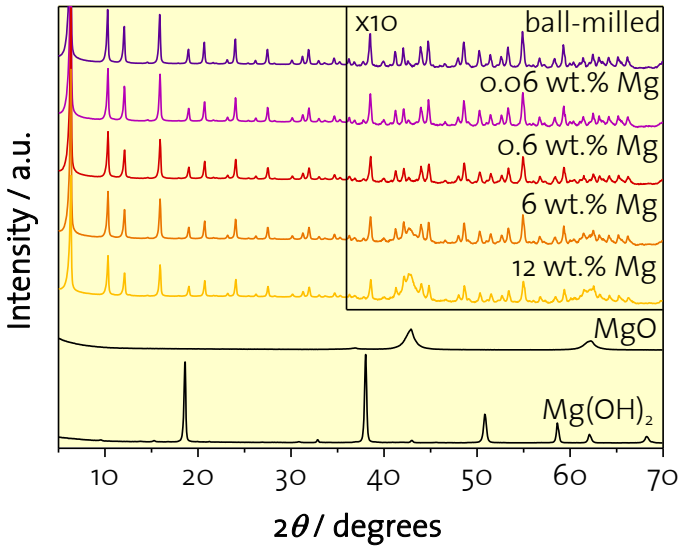


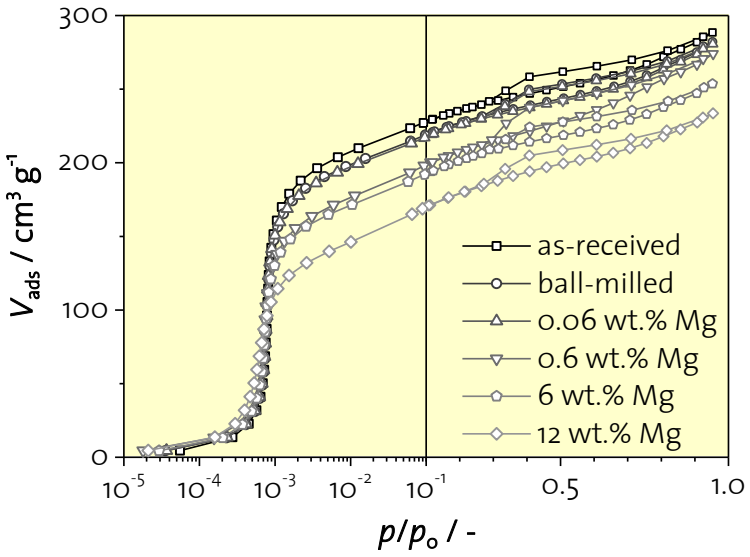


Mg-loaded USY zeolites

- X-ray diffraction and Ar sorption @ 77 K

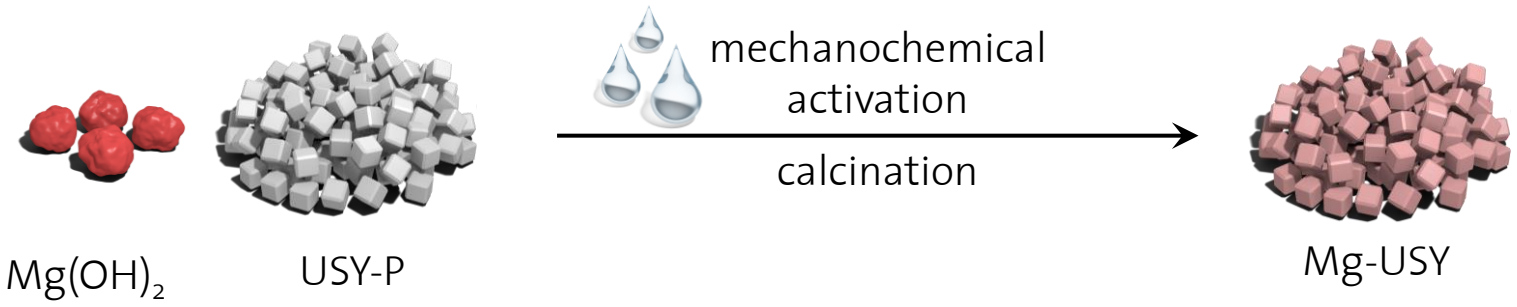


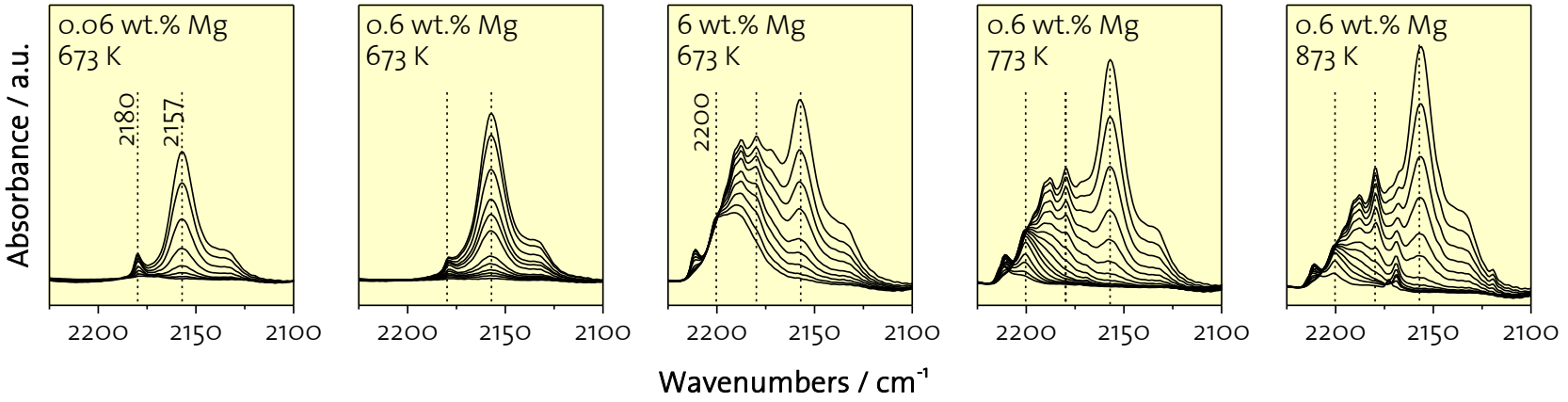




Mg-loaded USY zeolites

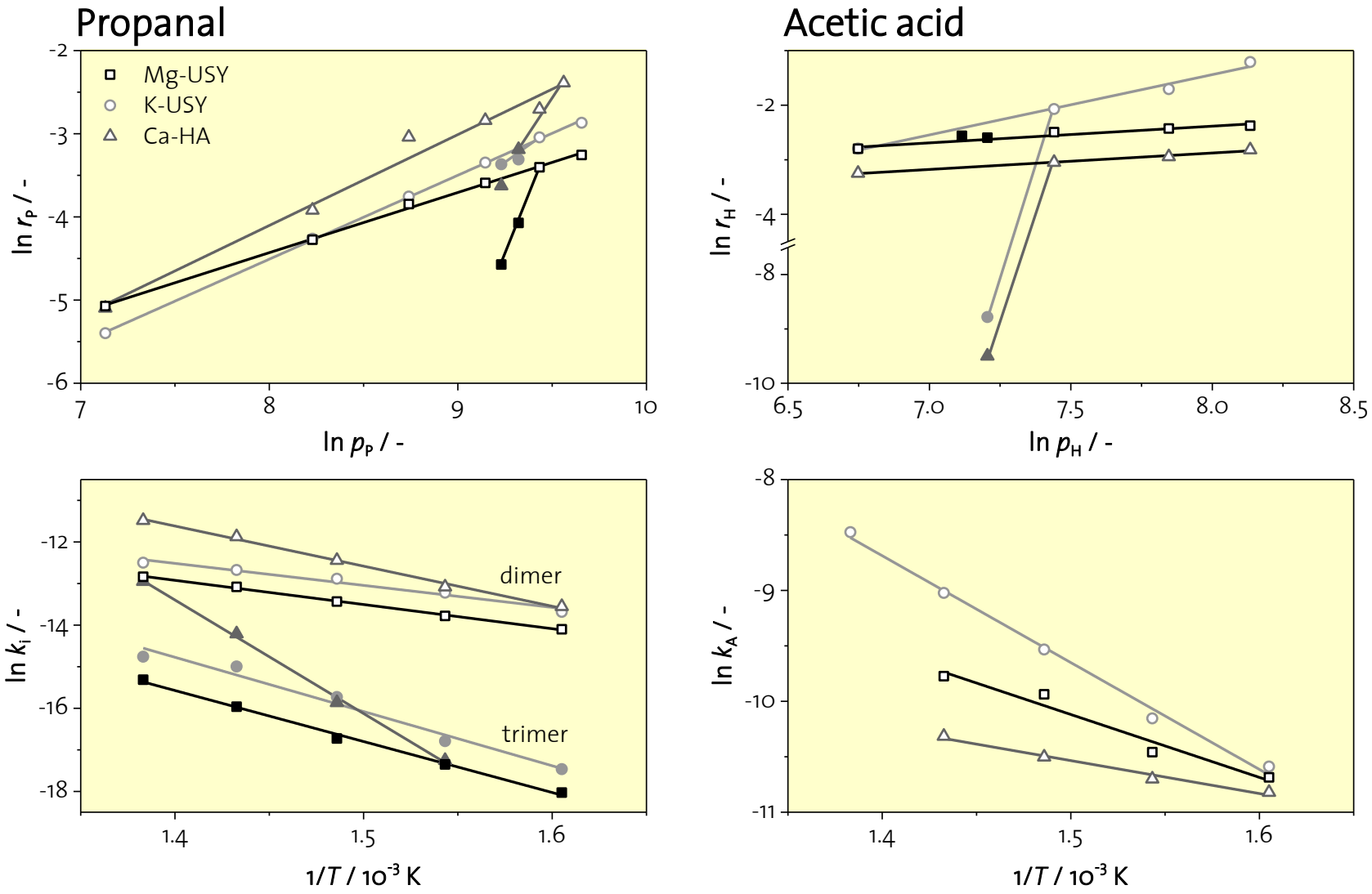
- Transmission-IR spectroscopy of adsorbed CO





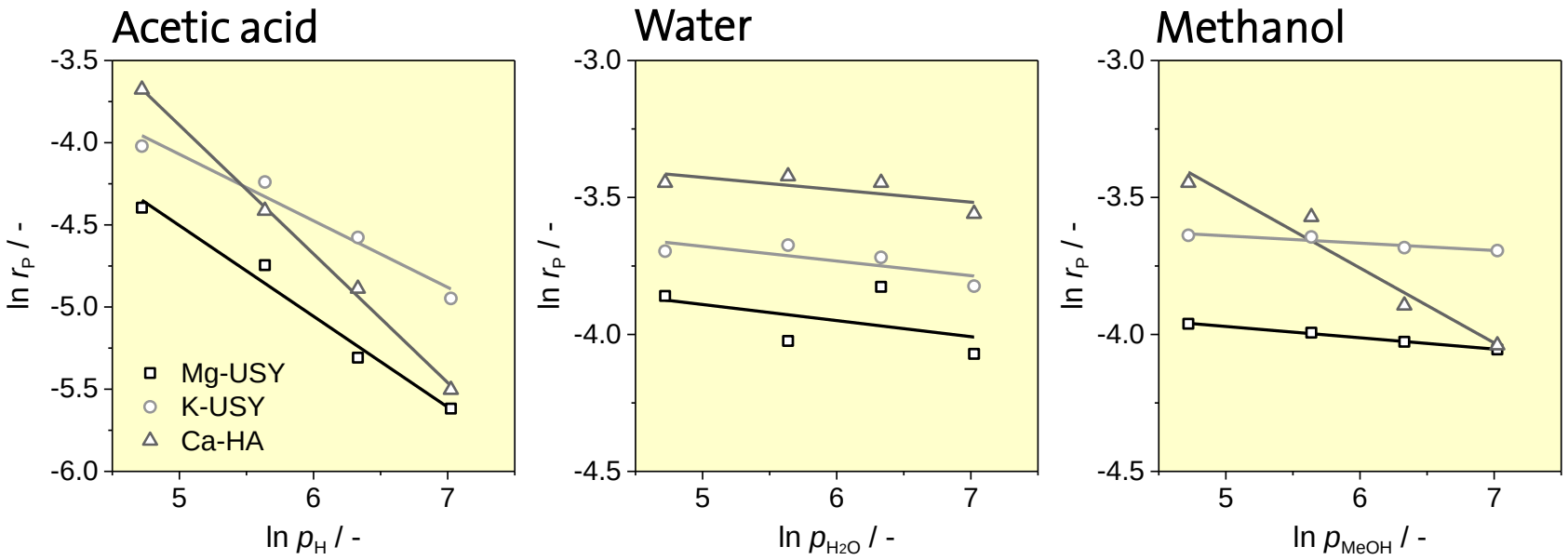
Kinetic studies with pure model compounds

- Reaction orders and activation energies



Kinetic studies with binary mixtures

- Reaction orders of the contaminant



Pure compounds			
(1) $P + * \leftrightarrow P^*$	$k_1; k_{-1}$	adsorption equilibrium of P	
(2) $P^* + P \rightarrow D^*$	k_2	surface reaction of P	
(3) $D^* \leftrightarrow D + *$	$k_3; k_{-3}$	desorption equilibrium of D	

Rate-limiting step	Assumptions	Reaction rate	Reaction order of P
(1)	- Steady state ($r_1 = r_2$) - Pseudo-equilibrium for step (3)	$r = r_1 = k_1 p_P \theta_* - k_{-1}\theta_P$ $= \frac{\frac{k_1 k_2 p_P^2}{k_{-1} + k_2 p_P}}{1 + \frac{k_1 p_P}{k_{-1} + k_2 p_P} + K_D p_D}$	$n_P = \frac{\partial \ln(r)}{\partial p_P} \underbrace{\frac{\partial p_P}{\partial \ln(p_P)}}_{p_P} = \frac{p_P(k_1 + k_2 + K_D p_D) + 2k_{-1}(1 + K_D p_D)}{p_P(k_1 + k_2 + K_D p_D) + k_{-1}(1 + K_D p_D)}$ Limiting cases: $\lim_{p_P \to 0} n_P = \frac{2k_{-1}(1 + K_D p_D)}{k_{-1}(1 + K_D p_D)} = 2$ $\lim_{p_P \to \infty} n_P = \frac{p_P(k_1 + k_2 + K_D p_D)}{p_P(k_1 + k_2 + K_D p_D)} = 1$
(2)	- Pseudo-equilibrium for steps (1) and (3)	$r = r_2 = k_2 \theta_P p_P$ $= \frac{k_2 K_P p_P^2}{1 + K_P p_P + K_D p_D}$	$n_P = 2 - \frac{K_P p_P}{1 + K_P p_P + K_D p_D}$ Limiting cases: $\lim_{p_P \to 0} n_P = 2 - \frac{0}{1 + 0 + K_D p_D} = 2$ $\lim_{p_P \to \infty} n_P = 2 - \frac{K_P p_P}{K_P p_P} = 1$
(3)	- Steady state ($r_2 = r_3$) - Pseudo-equilibrium for step (1)	$r = r_3 = k_3 \theta_D - k_{-3} p_D \theta_*$ $= \frac{k_2 K_P p_P^2}{1 + K_P p_P + \frac{k_2 K_P}{k_3} p_P^2 + K_D p_D}$	$n_P = 2 - \frac{K_P p_P + 2\frac{k_2 K_P}{k_3} p_P^2}{1 + K_P p_P + \frac{k_2 K_P}{k_3} p_P^2 + K_D p_D}$ Limiting cases: $\lim_{p_P \to 0} n_P = 2 - \frac{0}{1 + K_D p_D} = 2$ $\lim_{p_P \to \infty} n_P = 2 - \frac{2\frac{k_2 K_P}{k_3} p_P^2}{\frac{k_2 K_P}{k_3} p_P^2} = 0$

Binary mixtures			
(1)	$P + * \leftrightarrow P^*$	$k_1; k_{-1}$	adsorption equilibrium of P
(1')	$H + * \leftrightarrow H^*$	$k_{1'}; k_{-1'}$	adsorption equilibrium of H
(2)	$P + P^* \rightarrow D^*$	k_2	surface reaction of P
(2')	$H + H^* \rightarrow A^*$	k_2'	surface reaction of H
(3)	$D^* \leftrightarrow D + *$	$k_3; k_{-3}$	desorption equilibrium of D
(3')	$A^* \leftrightarrow A + *$	$k_{3'}; k_{-3'}$	desorption equilibrium of A

Rate-limiting step	Assumptions	Reaction rate	Reaction order of P
(2)	- Pseudo-equilibrium for steps (1), (1'), (3), and (3')	$r = r_2 = k_2\theta_P p_P = \frac{k_2 K_P p_P^2}{1 + K_P p_P + K_H p_H + K_D p_D + K_A p_A}$	$n_P = 2 - \frac{K_P p_P}{1 + K_P p_P + K_H p_H + K_D p_D + K_A p_A}$ Limiting cases: $\lim_{p_P \to 0} n_P = 2 - \frac{0}{K_H p_H + K_A p_A} = 2$ $\lim_{p_P \to \infty} n_P = 2 - \frac{K_P p_P}{K_P p_P} = 1$
(3)	- Steady state ($r_2 = r_3$) - Pseudo-equilibrium for steps (1), (1'), and (3')	$r = r_3 = k_3\theta_D - k_{-3} p_D \theta_* = \frac{k_2 K_P p_P^2}{1 + K_P p_P + K_H p_H + \frac{k_2 K_P}{k_3} p_P^2 + K_D p_D + K_A p_A}$	$n_P = 2 - \frac{2\frac{k_2 K_P}{k_3} p_P^2}{1 + K_P p_P + K_H p_H + \frac{k_2 K_P}{k_3} p_P^2 + K_D p_D + K_A p_A}$ Limiting cases: $\lim_{p_P \to 0} n_P = 2 - \frac{0}{1 + K_H p_H + K_D p_D + K_A p_A} = 2$ $\lim_{p_P \to \infty} n_P = 2 - \frac{2\frac{k_2 K_P}{k_3} p_P^2}{K_P p_P + \frac{k_2 K_P}{k_3} p_P^2} = 0$
(3')	- Steady state ($r_2 = r_3'$) - Pseudo-equilibrium for steps (1), (1'), and (3)	$r = r_3' = k_3'\theta_A - k_{-3}' p_A \theta_* = \frac{k_2' K_H p_H^2}{1 + K_P p_P + K_H p_H + \frac{k_2' K_H}{k_3'} p_H^2 + K_D p_D + K_A p_A}$	$n_P = \frac{\partial \ln(r)}{\partial p_P} \underbrace{\frac{\partial p_P}{\partial \ln(p_P)}}_{p_P} = 0$