ALD-Modified USY Zeolite Characterization Using Single-Event MicroKinetics

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Catalyst Modification

Modification of a commercial Pt/H-USY zeolite by Atomic Layer Deposition (ALD) making use of the $AlCH_3/H_2O$ process

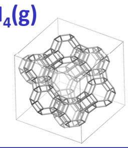
1. $||\text{-OH} + Al(CH_3)_3(g) \rightarrow ||\text{-O-}Al(CH_3)_2 + CH_4(g)$

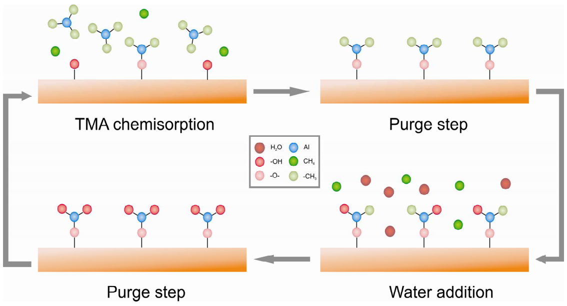
   $2||\text{-OH} + Al(CH_3)_3(g) \rightarrow (||\text{-O-})_2AlCH_3 + 2CH_4(g)$

2. $||\text{-CH3} + H_2O(g) \rightarrow ||\text{-OH} + CH_4(g)$

Parent material: CBV712

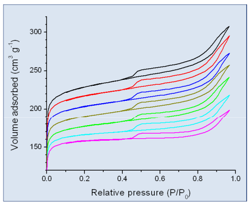
Si/Al = 5.8

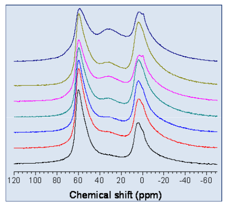




Catalyst Characterization §

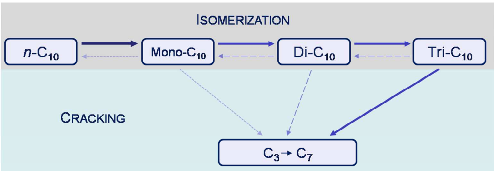
- Micropore volume → N_2 adsorption
- Acidity → Pyridine TPD
- Aluminium content → ^{27}Al MAS NMR





Single-Event MicroKinetic (SEMK) Modeling

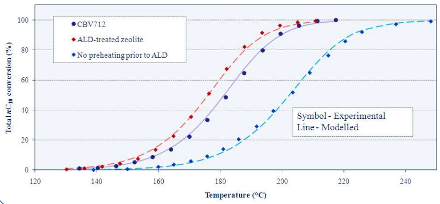
Hydrocracking experiments using *n*-decane

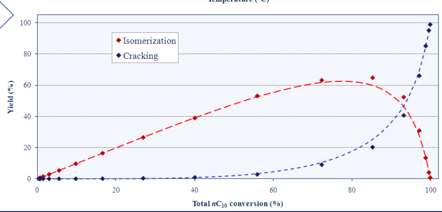


Performed in an isothermal plug flow reactor

$$\frac{dF_i}{dW} = R_i$$

W/F (s kg_{cat} mol^{-1})	T (K)	P (MPa)	H_2/HC
2520	403 - 533	0.45	375





$$r_{iso/cra}(m_1;m_2) = \frac{k_{iso/cra}(m_1;m_2) C_{sat} C_{acid} K_{prot} K_{deh} K_L p_P p_{H_2}^{-1}}{\left(1+\sum K_L p_P\right)\left(1+\frac{\sum C_{sat} K_{prot} K_{deh} K_L p_P p_{H_2}^{-1}}{1+\sum K_L p_P}\right)}$$

$$k_{iso/cra}(m_1;m_2) = n_e \tilde{k}_{iso/cra}(m_1;m_2)^{\dagger}$$

$\tilde{k}$ - unique rate coefficient of reaction family

n_e - number of geometrically independent ways in which the transition state can be formed → 'number of single events'

$m_1;m_2$ - type of reactant and product carbenium ion

Protonation enthalpy for ion formation estimated; $\Delta H_p(t) \approx \Delta H_p(s) - 30$ kJ mol^{-1}

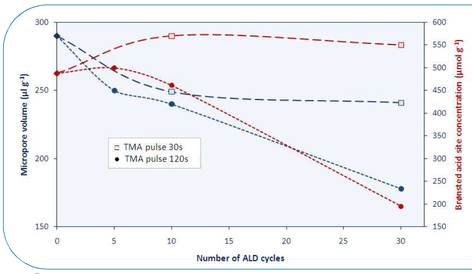
Effect of ALD on Catalyst Properties

Catalyst dried at 473 K for 6 h prior to ALD

TMA/H_2O pulse and purge times 30 or 120 s

Total number of ALD cycli 5, 10 or 30

ALD reaction temperature 473 K



TMA deposition in micropores ⇒ MV ↘

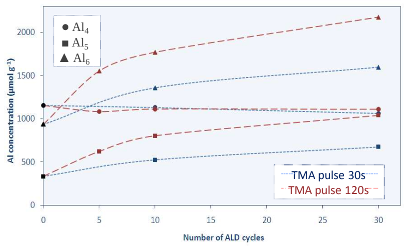
Creation of new acid sites, covered by extra-framework Al

⇒ C_{acid} ↗↘

Framework remains unharmed ⇒ Al_4 ≈

Reaction TMA and surface –OH, formation of Al_2O_3(s) through chemical vapour deposition

⇒ Al_5 ↗ and Al_6 ↗



ALD reaction temperature 573 K ⇒ steaming of zeolite ⇒ Al_4 ↘

No pretreatment catalyst ⇒ formation of weaker sites ⇒ -ΔH_p ↘

High purge times ⇒ longer reaction times H_2O ⇒ -ΔH_p ↘ , C_{acid} ↗

TMA pulse (s)	# ALD cycli	-ΔH_p (s) kJ mol-1	-ΔH_p (t) kJ mol-1
-	-	70.8 (± 0.1)*	101.6 (± 0.2)
30	10	72.8 (± 0.3)	102.4 (± 0.5)
30	30	72.0 (± 0.2)	100.4 (±0.4)
120	5	72.8 (± 0.3)	101.1 (± 0.5)
120	10	72.9 (± 0.2)	101.2 (± 0.5)
120	30	78.5 (± 0.3)	110.6 (± 0.3)

* 95% confidence region

Formation of new and possibly stronger sites
Inductive effect of extra-framework Al_2O_3(s)
} ⇒ -ΔH_p ↗

Improvement of hydrocracking activity explained through an increase in average acid site strength

Conclusions

- The single-event methodology has proven to be a useful tool in the assessment of catalytic modifications
- Each ALD parameter has a specific effect on the hydrocracking behavior of the catalyst through changes in micropore volume, Brønsted acid site concentration and average acid site strength
- The creation of new acid sites through ALD opens up the route towards the production of new active materials tailored to the requirements of a target reaction

Acknowledgements

This work was supported by the Research Board of Ghent University (BOF) and by the Interuniversity Attraction Poles Program – Belgian Science Policy.

§ S.P. Sree, J. Dendooven, T.I. Koranyi, G. Vanbutsele, K. Houthoofd, D. Deduytsche, J.A. Martens, and C. Detavernier, Cat. Sci. Techn. 1 (2011) 218-221.

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