A Comparative Study of ZSM-5 and β-Zeolites for Hydrocarbon Trap Applications under “Cold-Start” Conditions

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Motivation

- Significant attention has been paid to develop a method to treat automobile exhausts for the regulated emissions such as hydrocarbons (HCs) during the engine cold start.
- An effective solution is to employ suitable porous materials which can trap and retain hydrocarbons temporarily until automotive emission control catalysts are lit off.
- For this purpose, zeolites have been found to be a preferred type of adsorbent materials due to their thermal stability and affinity to HCs.
- Ag^+-exchanged ZSM-5 materials have shown superior adsorption properties and they are able to retain olefin and aromatic hydrocarbons well above the light-off temperature.

Objectives

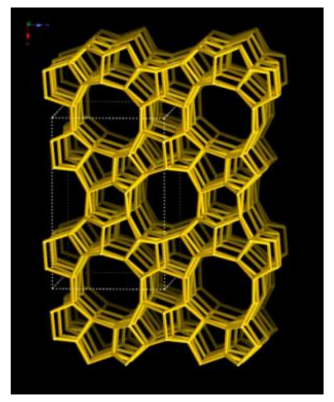
Our goal is to elucidate key factors controlling hydrocarbon adsorption/desorption performance of zeolite-based hydrocarbon traps for cold start emission control applications. Perform in-depth kinetic study of ZSM-5 and β-zeolites under the presence/absence of H_2O/CO_2/NO.

Experimental

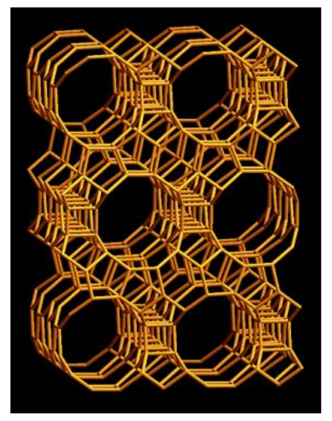
- Zeolites chosen based on industry feedback and literature survey
  - Components of actual commercial technology (conventional ICEs)
  - Most studied materials in academic settings

Large/medium pores allow easy HC transport

Zeolite type	SiO_2/Al_2O_3 molar ratio	Nominal cation form	Surface Area (m^2/g)
Beta	25	H^+	680
Beta	25	Ag^+	NM
Beta	300	H^+	620
Beta	300	Ag^+	NM
ZSM-5	30	H^+	405
ZSM-5	30	Ag^+	NM
ZSM-5	280	H^+	400
ZSM-5	280	Ag^+	NM

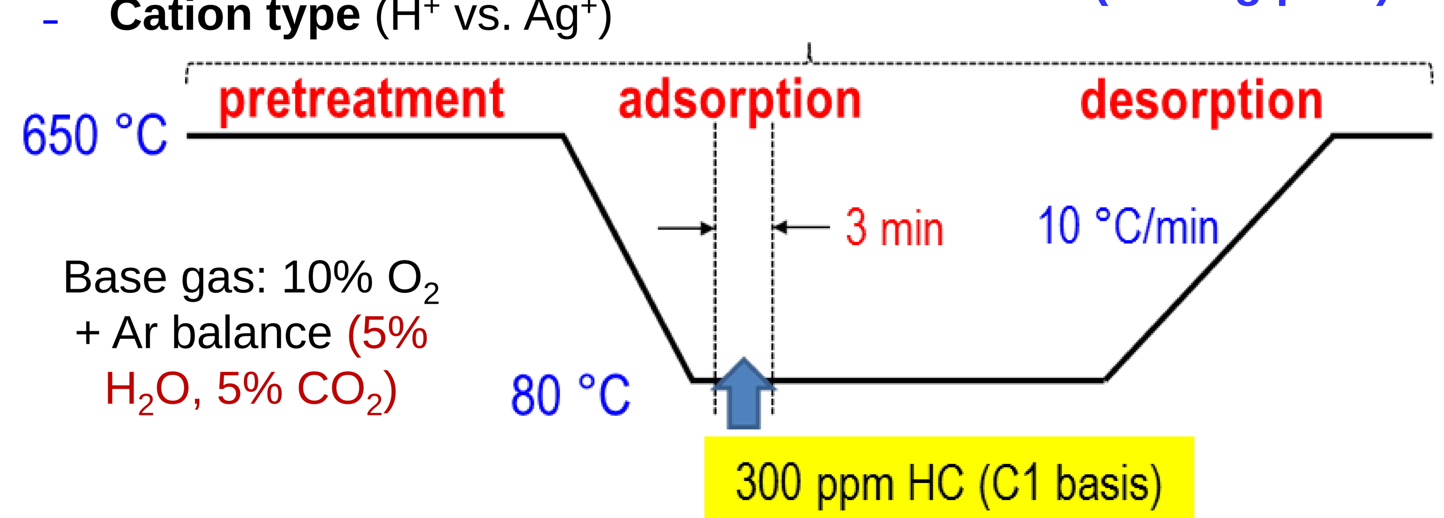


ZSM-5 (10-ring pore)



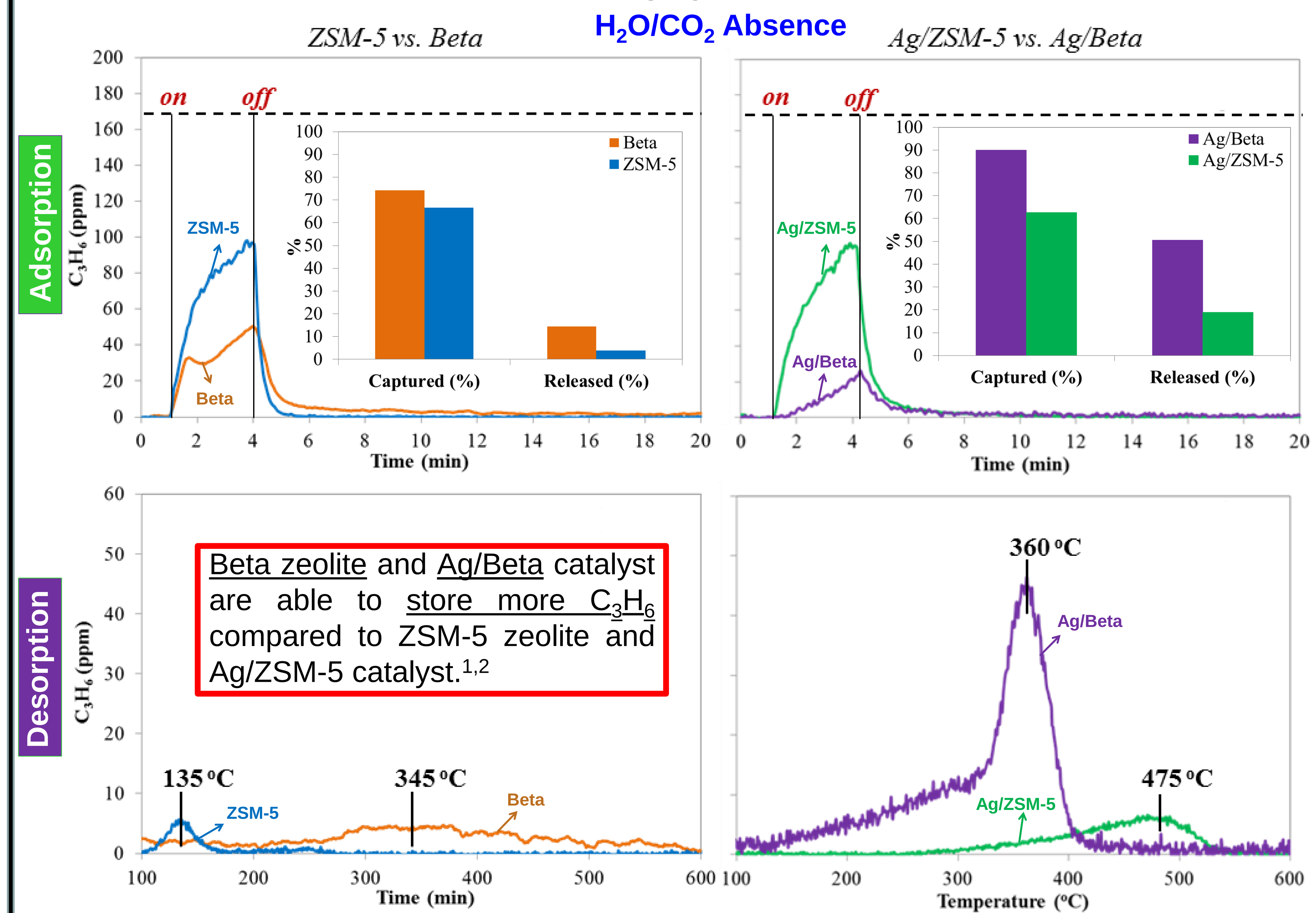
Beta (12-ring pore)

- Systematic variation of key zeolite properties
  - **Pore structure** (Beta vs. ZSM-5)
  - **Acidity** (low vs. high SiO_2/Al_2O_3)
  - **Cation type** (H^+ vs. Ag^+)



Trap loading: 25 mg/Total flow rate: 300 sccm/SV: 360,000 h^{-1}

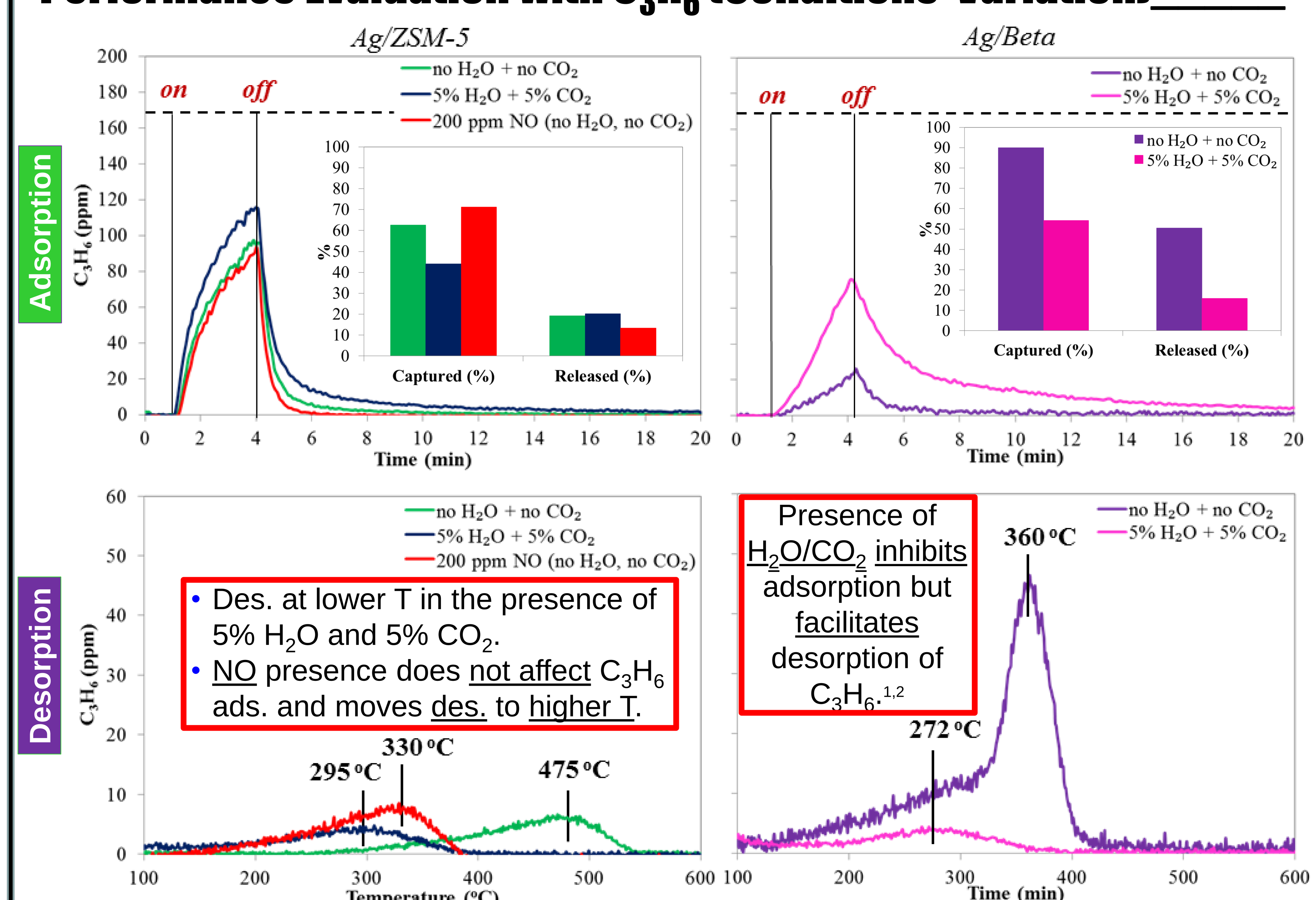
Performance Evaluation with C_3H_6 (Composition Variation)



- In the presence of Ag:
  - C_3H_6 desorption is facilitated and
  - C_3H_6 desorption is present at higher temperatures compared to the zeolite only samples

5 wt% Ag loading obtained for both zeolite types (low SiO_2/Al_2O_3 cases)

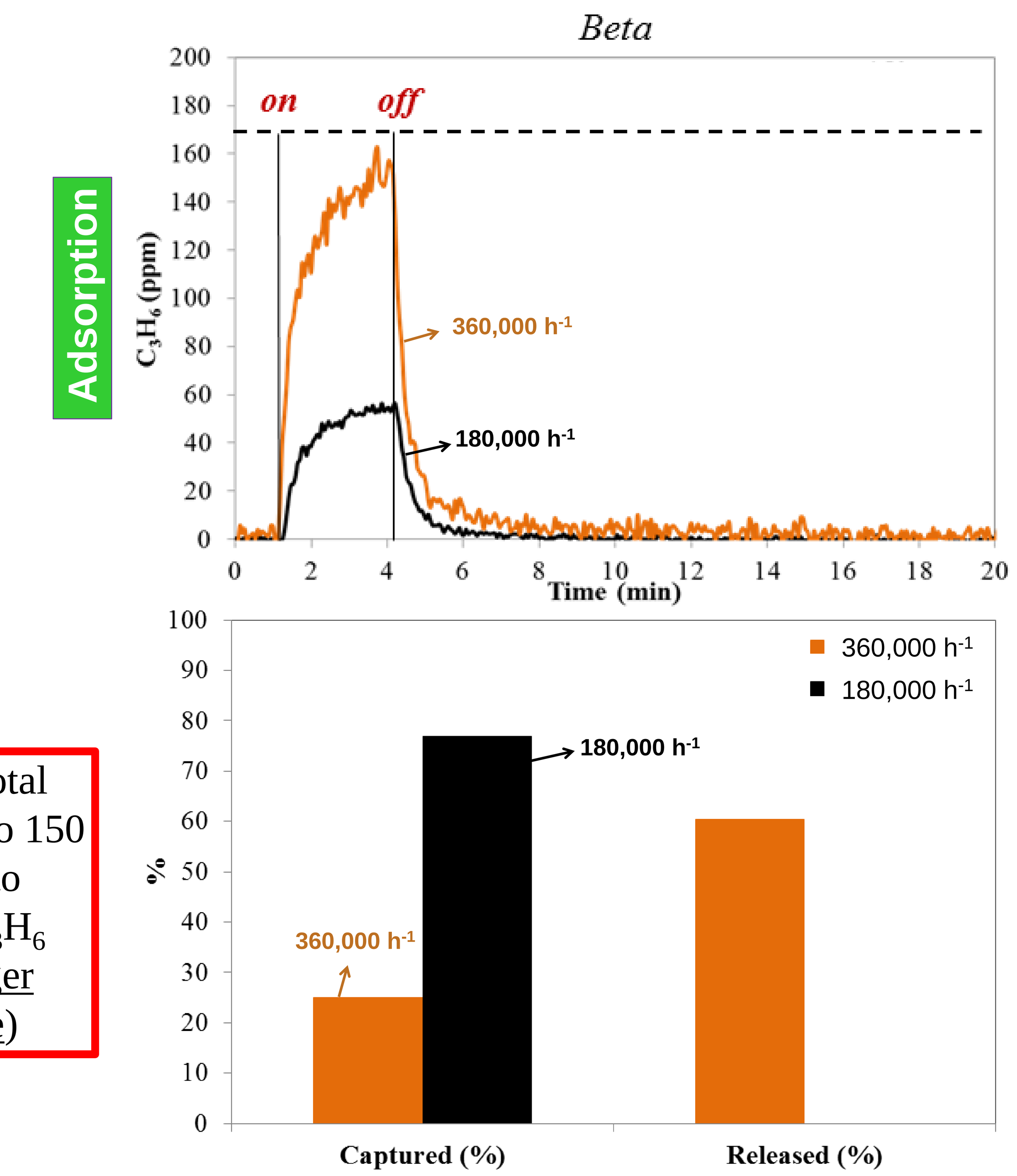
Performance Evaluation with C_3H_6 (Conditions Variation)



1) Takamitsu, Y., Ariga, K., Yoshida, S., Ogawa, H., Sano, T. Bull. Chem. Jpn. 85(8), 869 (2012)
2) Moden, B., Donohue, J. M., Cormier, W. E., Li, H.-X. Top. Catal. 53, 1367 (2010)

C_3H_6 Adsorption for different Total flows

C_3H_6: 167 ppm, O_2: 10%, H_2O: 5%, CO_2: 5%

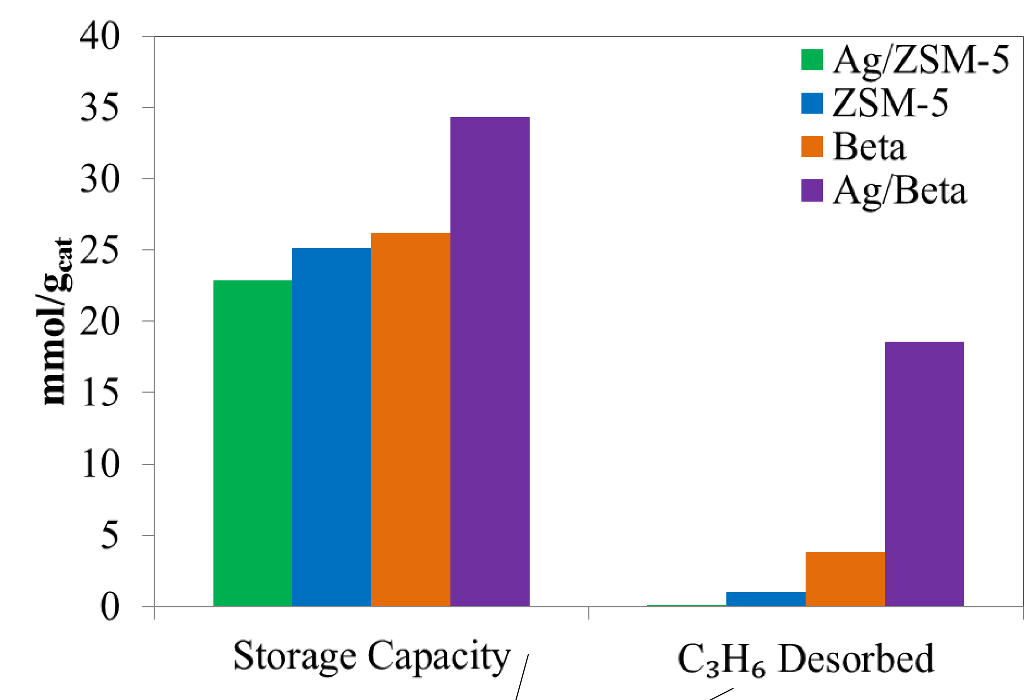


Decrease in total flow from 300 to 150 sccm leads to increase in C_3H_6 storage (longer contact time)

Conclusions

- **Beta** Zeolite is able to **store more C_3H_6** compared to **ZSM-5**

H_2O presence:
- **Inhibits** C_3H_6 storage
- CO_2 impact minor



The HC adsorption is not straightforward. Decomposition and other reactions of C_3H_6 likely occur.

- The silver exchanged ZSM-5 and β-zeolites - compared to H^+ counterparts - exhibited an increased storage and desorption of propylene.
- The presence of NO over the Ag/ZSM-5 catalyst showed no impact on propylene adsorption.

Acknowledgments

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