Structural Interconversion Between Agglomerated Palladium Domains and Isolated Pd^{2+} Cations in Chabazite Zeolites

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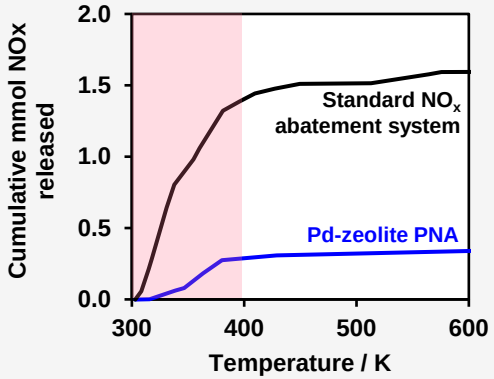
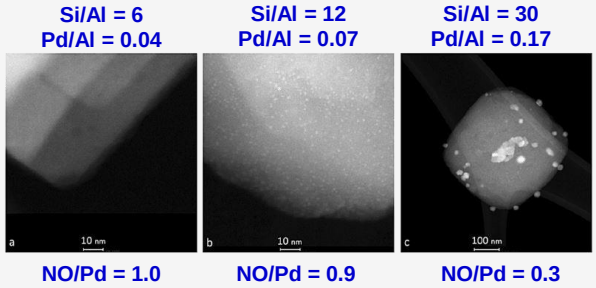
Transient vehicular conditions motivate understanding of Pd structures

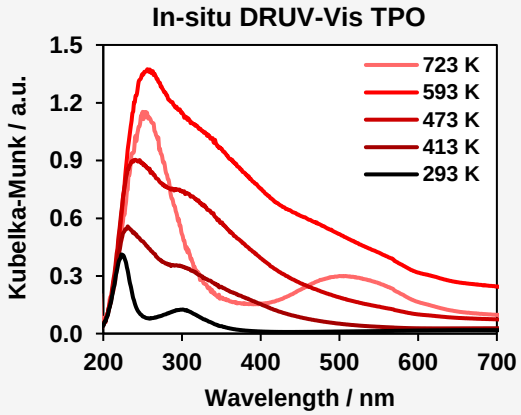


- Majority of NO_x released below 400 K[1]
- Pd-zeolites are effective passive NO_x adsorbers (PNA)[2]



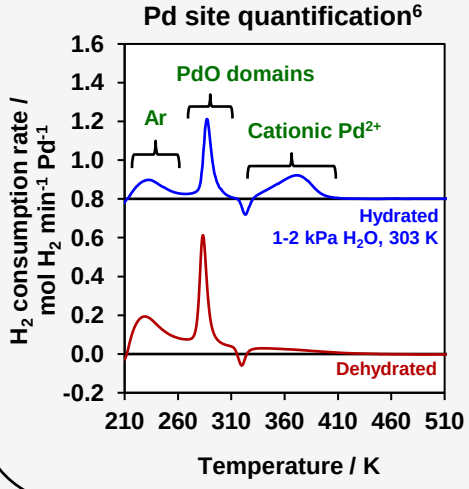
- Single-site Pd^{2+} cations are purported PNA storage site
- Bulk Al density influences formation of Pd^{2+} cations[3]
- What are the mechanisms of Pd^{2+} cation formation?
- How does zeolite material properties and treatment conditions influence formation of Pd^{2+} cations?

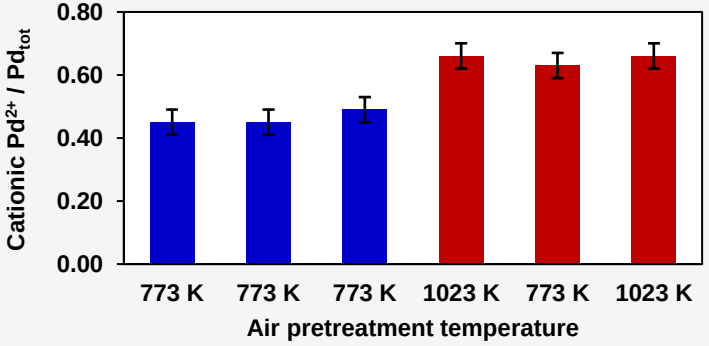
Formation of single-site Pd^{2+}



$[Pd(NH_3)_4]^{2+}$ agglomerates before converting to single-site Pd^{2+} in air[4,5]

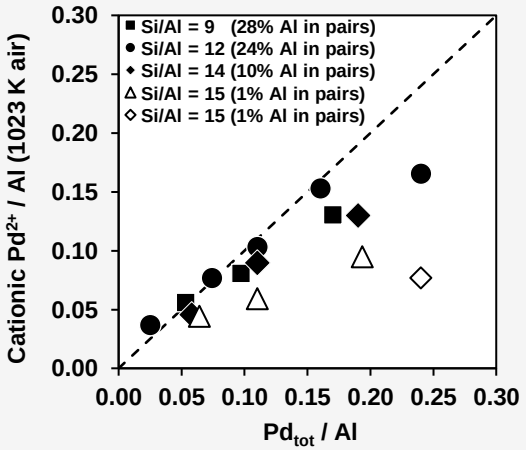
Reversible formation of Pd^{2+} infers changes in spatial distribution





- Hydrating Pd^{2+} cations allows for accurate quantifications[7]
- 1023 K air increased the reversible formation of Pd^{2+} cations likely by changing the spatial distribution of Pd

Atomic-scale Al properties



6-MR paired Al sites (quantified by Co^{2+} titration)[8] are preferred Pd^{2+} site

[1]Murata et al., SAE Int. Fuels Lubr., 8 (2015) 454-459; [2]Chen et al., US Patent: US10005075B2; [3]Khivantsev et al., Angew. Chem., 130 (2018) 16914-16919; [4]Spielbauer et al., Langmuir 9 (1993) 460-466; [5]Shimizu et al., J. Cat. 195 (2000) 151-160; [6]Homeyer and Sachtler, Appl. Catal. 54 (1989) 189–202, [7]Lee et al., App. Cat. B: Env. 227 (2020) 119190; [8]Di Iorio et al., J. Am. Chem. Soc. 142 (2020) 142 4807–4819

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The effects of CO co-feed on a Pd/BEA Hydrocarbon Trap: A Combined Reactor and DRIFTS Study of Pd Speciation

Ryan Zelinsky and William Epling – University of Virginia

Motivation – Hydrocarbon Emissions

Experimental Methods

Synthesis & Experimental

NH_4/BEA
Si/Al = 38

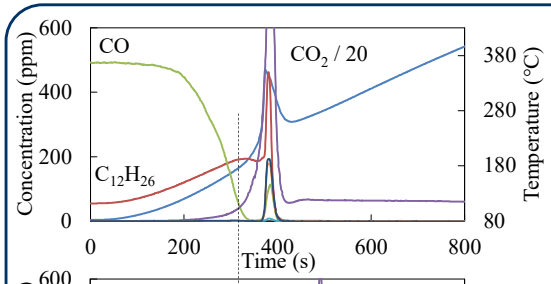
Calcine in Air

H/BEA

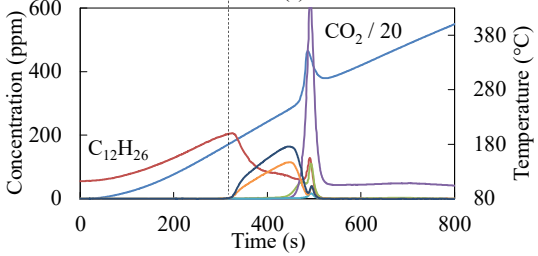
Wetness Impregnation

1 wt% Pd/BEA

Pd/BEA – CO Co-Feed

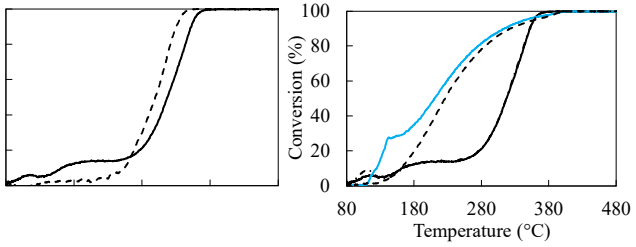


With CO cofed, hydrocarbon oxidation light-off and desorption at lower T

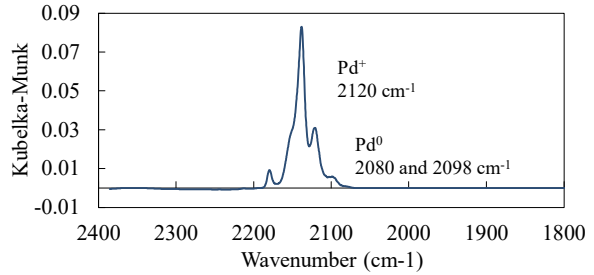


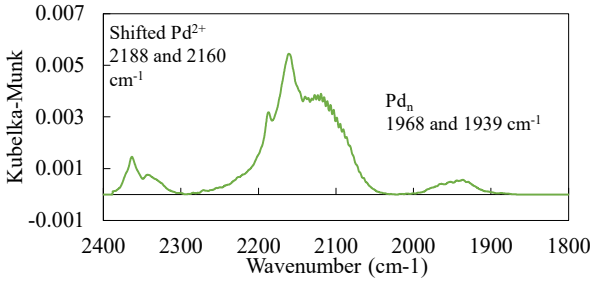
With no CO, more HCs desorb, coming from dodecane cracking, less are oxidized

Without exchanged Pd, CO co-feed has no effect on trap behavior



CO DRIFTS





Conclusions

- CO co-feed in the presence of H_2O leads to a change in hydrocarbon oxidation light-off behavior on Pd/BEA.
- CO pretreatment in dry conditions leads to no change in oxidation behavior, however a pretreatment of CO and H_2O leads to oxidation behavior similar to a constant feed of these species with C_2H_4.
- DRIFTS studies revealed that after treatment at 80°C in CO and H_2O, several ionic Pd species disappeared from the spectrum while features indicative of particulate Pd arose, which may be the culprit of changed oxidation behavior.

Acknowledgements

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