INVESTIGATION OF METAL ION MOBILITY UNDER EXPOSURE TO DEACTIVATING AGENTS

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Abstract

Interest in metal loaded zeolites as hydrocarbon adsorbents has increased significantly over the last few years. These catalysts however suffer from deactivation due to various processes such as sintering, poisoning, and active site transformation. In this work, a Pd/BEA sorbent was tested under various feed conditions to probe its efficacy in adsorbing hydrocarbon fuels while exposed to deactivating agents, with the model hydrocarbon being ethylene. Deactivation under these feed conditions was observed and further studied using diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). Ethylene uptake was partially inhibited by CO and H_2O when fed separately. When both were added, the loss in ethylene uptake was 90% relative to the condition with no H_2O or CO. DRIFTS characterization shows that some form of oxidized Pd was reducible to Pd^0 by CO at 80 °C only in the presence of H_2O. Further, this reduction appears reversible by high temperature oxygen treatment. We speculate that this reduction of ionic Pd is what results in the significant loss in ethylene adsorption capacity.

Introduction

Zeolite based catalysts are a very important material for many industrial purposes. They are used in chemical synthesis as catalysts for hydrocarbon cracking[1], oligomerization[2], and methane coupling[3]. In the automotive industry, they are used in aftertreatment systems for NOx reduction[4], NOx adsorbers[5], and hydrocarbon trapping[6]. Their efficacy in performing such a wide variety of reactions is due to their unique properties as both solid acids and molecular sieves. With silicon substitution for aluminum in the framework, a charge imbalance is produced which serves as a site for a Brönsted acid if H^+ is the balancing cation, or as a metal ion exchange site. Their unique properties as a molecular sieve are due to the typical pore sizes in zeolites being on the order of the kinetic diameter of many molecules.[7] This allows selective adsorption of target molecules with exclusion of others depending on the specific zeolite crystal structure.

Active sites are often introduced to the zeolite in the form of ion-exchanged metals. These active centers facilitate the interactions between reaction molecules, while zeolite pore dimensions allow for selectivity towards desired products. While unique chemistries can be performed in the conditions within the zeolite pore, challenges arise in predicting zeolite stability. For example, Luo et al. found that after hydrothermal aging, a technique often used to simulate the lifetime of an automobile aftertreatment catalyst, ZCuOH sites in Cu/SSZ-13 transformed into Z2Cu sites.[4] Further, performance degradation was observed in Pd/SSZ-13 and Pd/BEA passive NO_x adsorbers from high temperature CO exposure. The performance loss was attributed to irreversible reduction of ionic Pd active centers to metallic Pd.[8]

Text adapted from and figures reprinted from: Zelinsky, R. & Epling, W. S. Effects of co and h2o co-feed on the adsorption and oxidation properties of a pd/bea hydrocarbon trap. *Catalysts* **11**, 1–14 (2021).

Since recent literature points to high metal ion mobility, whether it be active site transformation or reduction and migration out of the pores, it is important to employ direct methods which can track the active metal speciation. In this work, we utilize Pd/BEA as a hydrocarbon trap and study a deactivation mechanism which has not yet been described in the literature. When exposed to CO at 80°C, even in the presence of 12% O_2, severe losses (>90%) in ethylene storage were observed. We show that the loss in storage cannot be entirely attributed to competitive adsorption, so we employed temperature programmed reduction (TPR) and DRIFTS to characterize changes in the Pd speciation at 80°C which may have led to the loss in ethylene storage.

Experimental

Catalyst Synthesis

In this study, zeolite beta in the ammonium cation form, NH_4^+/BEA, was purchased from a vendor (Zeolyst). The powder was treated at 500°C in air for 4 hours to obtain the H^+ form, denoted H/BEA. To obtain Pd/BEA, a palladium precursor salt ($Pd(NO_3)_2$, Sigma Aldrich) was dissolved in water and added dropwise to the dry catalyst powder. The catalyst was then treated at 600°C in air for 4 hours.

The Pd/BEA powder was then washcoated onto cordierite monoliths. To prepare the washcoat, a slurry was formed by mixing the catalyst with water and a colloidal alumina binding agent (Nyacol Al20). The slurry was placed in a glass tube and the monolith dipped into the slurry and dried. This process was repeated until the monolith was loaded with the appropriate amount of catalyst by mass. Finally, the monoliths were dried and treated at 600°C in air for 4 hours.

Hydrogen TPR

Hydrogen temperature programmed reduction (H_2 TPR) is a technique which allows one to probe the reducibility of the catalyst as a function of temperature. H_2 TPR was performed in house on an AutoChem II 2920 chemisorption analyzer. The powder was placed in a glass tube along with quartz wool and a thermocouple. First, the catalyst was pretreated in 10% O_2/He at 500°C for 45 minutes. Next, the catalyst was cooled down to 50°C and exposed to 5% H_2/He until the thermal conductivity detector (TCD) signal was stabilized. Finally, a temperature ramp of 10°C/min was applied while H_2 was flowing and the TCD signal was mapped to the temperature.

Reactor Tests

To test the adsorption capacity of the Pd/BEA, experiments were performed on a bench top reactor system. The catalyst was placed into a quartz tube. The tube was placed into the benchtop furnace (Lindberg Blue M) with thermocouples in both the upstream and downstream ends to measure temperature changes. The reactor is outfitted with two automated four-way valves and a bypass line which allows for preparation of the gas mixture before introduction to the catalyst. This setup allows for precise measurement of the time which adsorption begins over the catalyst.

To measure the gas concentrations, an MKS 2030 series Fourier transform infrared spectrometer (FTIR) was attached downstream of the catalyst and bypass. Table one gives the gas concentrations used in this study.

Table 1. Feed gas concentration for each species.

Species	***Concentration***
N_2	Balance
O_2	12%
H_2O	6%
CO	500 ppm
C_2H_4	200 ppm

Each species was supplied using gas cylinders (Praxair). To introduce water, a controlled evaporator mixer (CEM) system (Bronkhorst) was employed. The CEM allows for precise amounts of liquid water to be vaporized and mixed with the gas stream. The gas hourly space velocity for these experiments was 30,000 hr^{-1}.

Before each experiment, the catalyst was treated in 12% O_2/N_2 at 600°C for 1 hour to regenerate the catalyst from any previous experiment. This treatment serves to both remove carbonaceous deposits from the zeolite and to reoxidize Pd active sides. After the oxygen pretreatment, the temperature was stabilized to 80 °C. Once the feed mixture was stable and verified in the bypass, the valves were switch and the adsorption began.

DRIFTS Studies

Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was used to probe the Pd speciation under reaction conditions. First, powder Pd/BEA was packed into the Harrick Scientific Praying Mantis reaction chamber, equipped with ZnSe windows. The reaction chamber was placed into the Nicolet iS50 FT-IR instrument and purged overnight in He. The experiments began with a pretreatment at 500°C in 10% O_2/He to regenerate the catalyst and remove any carbonaceous deposits. Next, the cell was cooled to 80°C in He. Two experiments were performed, one with no water and the other with 2% water. For the dry experiment, the background was taken in He. For the wet experiment, the background was taken in 2% H_2O/He. Immediately following the background, 1000 ppm CO was introduced to the catalyst and sample spectra were taken initially every minute for 10 min followed by every 5 min until an hour elapsed. For each reported spectrum, 32 spectra were averaged.

Results and Discussion

Ethylene Adsorption

Figure 1 shows the adsorption curves of ethylene over Pd/BEA under four experimental conditions. Here, the adsorption begins at T = 50 s when the bypass is switched to the reactor. Table 2 summarizes the ethylene uptake totals for each experiment. Under these conditions, ethylene uptake mainly occurs over both Brønsted acid sites and cationic Pd. In the absence of H_2O, Brønsted acid sites interact with π-electrons in ethylene to form a bond, however when H_2O is present in percent level concentrations it outcompetes ethylene for these sites.[9,10] Over Pd ions, the electrons in ethylene form a π-complex with Pd which results in chemisorption.[9,11]

Here, when H_2O was included in the feed, a loss of ethylene/Pd ratio of about 50% was observed, decreasing from 3.6 to 1.8. This is likely due to the aforementioned competitive adsorption between H_2O and ethylene over Brønsted acid sites.

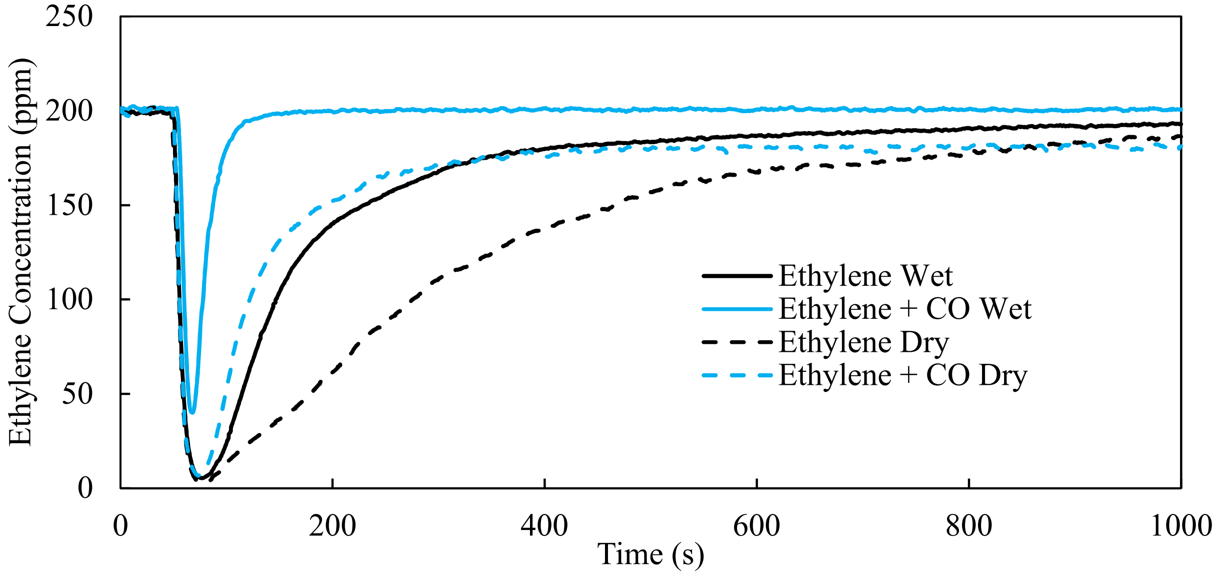

Figure 1. Ethylene uptake over 1% Pd/BEA with and without CO co-feed in wet and dry conditions. Adsorption begins at T = 50 s. (200 ppm ethylene, 0 or 500 ppm CO, 0 or 6% H_2O, 12% O_2, balance N_2).

Table 2. Ethylene uptake and ethylene/Pd ratio for each experiment.

Experiment	Ethylene uptake (µmol)	Ethylene/Pd ratio
Ethylene Dry	47	3.6
Ethylene + H_2O	24	1.8
Ethylene + CO Dry	31	2.4
Ethylene + H_2O + CO	3.5	0.27

The addition of CO also led to loss of ethylene uptake at 80 °C, with a decrease in ethylene/Pd ratio by about 1.2. We speculate that inclusion of CO in dry conditions leads to competitive adsorption over the ionic Pd sites responsible for ethylene uptake. Further, the addition of H_2O and CO lead to almost complete loss of ethylene uptake. According to Table 1, under CO and H_2O co-feed, the catalyst displays ~7.5% of the ethylene uptake compared with the experiment with no H_2O and no CO. By combining the effects of H_2O and CO separately, these account for a loss of ~83% of ethylene storage. The remaining discrepancy, roughly 10% of total ethylene storage, is left unaccounted for.

Hydrogen TPR

To characterize the reducibility of the as-synthesized catalyst, we employed hydrogen TPR. Here, we were able to identify the existence of a particulate phase in the fresh catalyst. Figure 2 shows the H_2 TPR plot for the 1% Pd/BEA catalyst.

The negative peak at 50–80 °C represents H_2 generation which stems from decomposition of PdH. PdH is formed when H_2 reacts with Pd particles during initial H_2 exposure at low temperatures.[12] The peak at 80–150 °C and the high temperature peaks at ~450 °C correspond to different forms of ionic Pd.[5,13] These results indicate that the initial sample contains both ionic Pd and large Pd particles, each if which may have different interactions with the feed mixture.

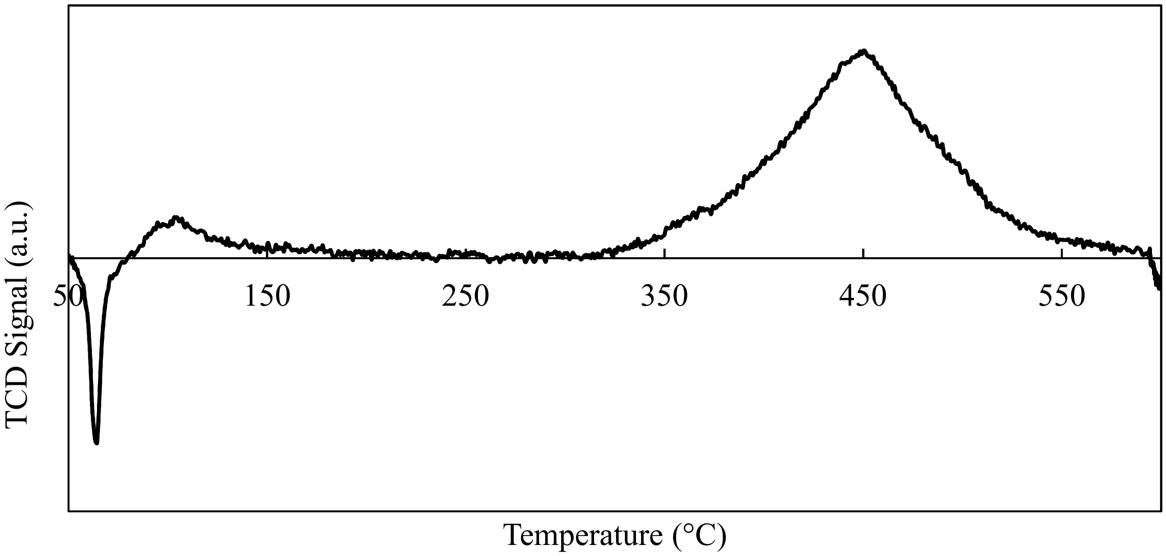

Figure 2. Hydrogen TPR for 1% Pd/BEA (5% H_2/He, Ramp rate = 10 °C/min) Pretreatment: 500 °C in 10% O_2/He for 60 min.

It is important to note that this is the expected Pd/BEA state after several adsorption-desorption cycles. Recent literature has indicated that a catalyst which has been exposed to CO at high temperatures will experience partial irreversible Pd agglomeration, resulting in a mix between cationic Pd and agglomerated particulate Pd.[5,8,13]

CO DRIFTS

To investigate the Pd speciation when co-feeding CO and H_2O, we used infrared spectroscopy with CO as the probe molecule. We conducted four experiments sequentially, with and without H_2O in the feed. The results, shown in Figure 3, indicate that multiple CO–Pd species exist on the Pd/BEA catalyst at 80 °C. The spectrum labeled 'Dry 1′ displays features at 2214 and 2194 cm^{-1} which correspond to CO bound to 'super electrophilic' Pd^{2+} which was described by Khivantsev et al to form a $(CO)_2$-Pd^{2+} dimer.[14] Other spectral features corresponding to CO–Pd^{2+}, appear at 2180, 2173, 2153, and 2140 cm^{-1}. The feature appearing at 2120 cm^{-1} is often attributed to CO–Pd^{+}.[15–19] Finally, two peaks at 2098 and 2080 cm^{-1}, which correspond to linearly bound CO–Pd^0, appear after approximately 30 min exposure. These are likely formed upon reduction by the probe molecule, CO, during exposure.[16,18] Under dry conditions no peaks appear in the range of 1800–2000 cm^{-1}.

Under wet conditions, some peaks corresponding to ionic Pd disappear, while others corresponding to metallic Pd emerge. In the 'Wet 2′ spectrum, the only remaining peaks which correspond to Pd^{2+} are at 2153 and 2140 cm^{-1}. Peaks at 2098 and 2080 cm^{-1} remain, but again do not populate until much later times, after 30 min exposure to CO and H_2O. Most interestingly, peaks at 1920 and 1950 cm^{-1} first appear under these conditions. These correspond to bridging CO–Pd_2^0 which can only occur over Pd particles.[18–22] The following two spectra, "Dry 3" and "Wet 4", demonstrate the ability to replicate the same CO–Pd environment after multiple cycles.

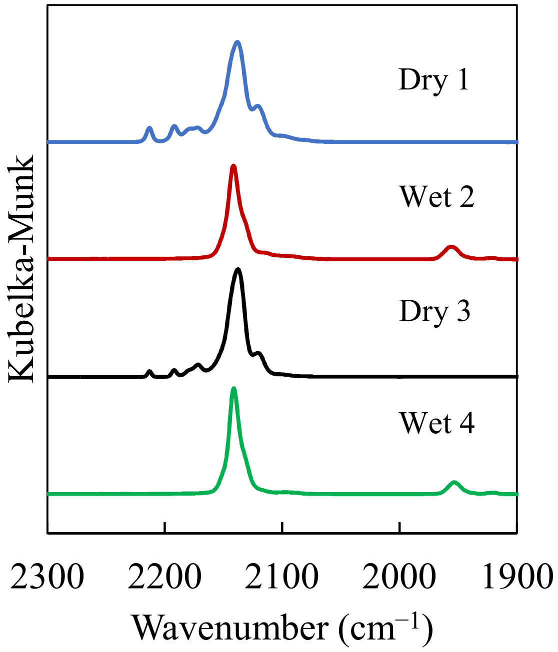

Figure 3 CO DRIFTS at 80 °C with four consecutive experiments switching between dry and wet conditions, with O_2 pretreatments at 500 °C in between each. Exposure time = 30 min. (1000 ppm CO, 2% H_2O, 10% O_2, balance He).

These results suggest an interconversion between ionic Pd^{2+} and Pd particles which may be the culprit of the loss in ethylene storage. The existence of bridging CO-Pd_2 suggests that the reduced Pd agglomerated to form Pd particles, as these features cannot exist over Pd single atoms. This means the Pd was removed from the ion-exchange site and migrated to other Pd atoms.

Further study is required on a model catalyst to confirm this hypothesis however because we have not isolated the ionic Pd from particulate Pd which exists on the fresh catalyst. In addition, further characterization of the Pd species by TPR after exposure to CO and H_2O would aid in confirming this hypothesis. These considerations are currently being tackled in ongoing studies.

Conclusions

In this work, we conducted hydrocarbon trap experiments over Pd/BEA and varied the feed composition to test the effects of H_2O and CO. Ethylene uptake was significantly affected by both. When H_2O and CO both existed in the feed, ethylene uptake was decreased by over 90% compared to the uptake with both absent. Ethylene uptake loss when CO is present is likely due to competitive adsorption to ionic Pd sites, and ethylene uptake loss when H_2O is present is likely due to competitive adsorption to Brønsted acid sites. When CO and H_2O are co-fed, however, the larger decrease in ethylene uptake occurred which may result from the formation of reduced Pd which is inactive in ethylene uptake under these conditions.

CO-DRIFTS results show that under conditions which include H_2O, peaks arise which indicate bridging CO–Pd_2^0. These represent a reduced Pd phase which we speculate formed by reduction of ionic Pd storage centers by CO in the presence of H_2O at 80°C.

Acknowledgements

The authors would like to thank the Virginia Space Grant Consortium (VSGC) for funding this research for the academic year 2020-2021.

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(doi:10.3390/catal11030348)

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