Supported Metal Catalysts for Pump Oil Detritiation

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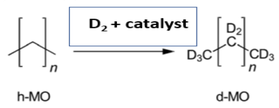
Background

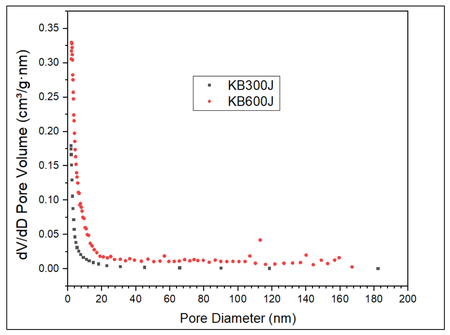
- Tritium is a very useful radioactive isotope in fusion power plants.
- However, the vacuum pumps oil used in these fusion facilities could be contaminated by the tritium through isotope exchange between the tritium (T) and the protium (H) of the pump oil.
- The decay of this tritium from the oil backbone can cause breakdown of the oil into small fragments and could result in the formation of formation of more toxic tritiated species than the tritium gas T_2. This potentially poses threat to the environment.
- As a matter of fact, there has been minimal efforts to purify and recycle tritiated oils. Direct disposal wouldn't be feasible because there is a large tritium inventory in fusion plants. So, our goal is to detritiate the oil and recycle them.
- Due to the toxic nature of these tritium species, we are utilizing deuterium as a simulant.
- Since the ease of deuterium uptake in oils is tantamount to the ease of detritiation, we have studied the catalytic deuteration of an aliphatic oil (LVO500 mineral oil), using Pt and Pd catalysts supported on carbons such as Ketjen black 300J and Ketjen black 600J.



- Our hypothesis is that highly dispersed metal particles on carbon supports will have activity for thermal and electromagnetic detritiation catalysts.
- Overall, we have compared performance of these catalysts based on metal type, particle size and support oxidation level. We have also compared the performance of the most active catalyst to a commercially available 50% Pt/Tanaka carbon.

Methodology

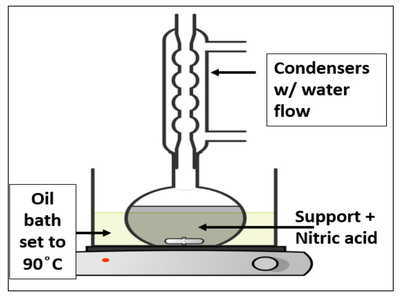
Support BET Analysis



- The BET surface area of the two supports used was determined using N_2 physisorption.
- KB600J has a surface area of 1360m²/g while KB300J has a surface area 720m²/g.
- KB600J appears to have larger amount of mesopores compared to KB300J with average pore diameter 4.3nm and 9.0nm respectively

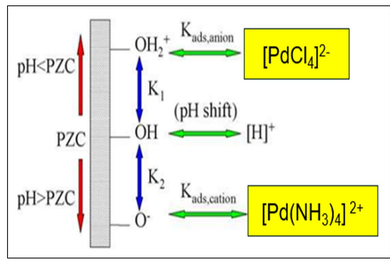
Support Oxidation/PZC Measurement

- Different support oxidation levels on KB300J support was achieved by boiling the support in varying nitric acid concentration.
- PZC 2, 6.7 and PZC 9 were achieved as measured using a spear tip pH probe at incipient wetness condition of the support.
- Low PZC supports corresponds to more surface oxygen groups.



Catalyst Synthesis

Strong Electrostatic Adsorption (SEA) and Dry impregnation (DI)



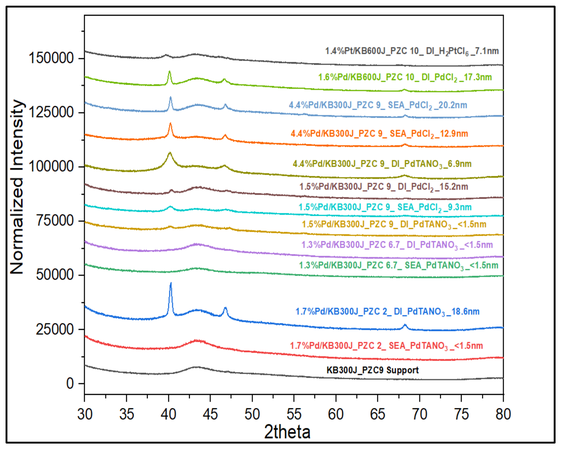
- The catalysts were synthesized either by conventional dry impregnation method or by strong electrostatic adsorption where the support is charged up to allow for an oppositely charged precursor adsorption.

Oil Deuteration

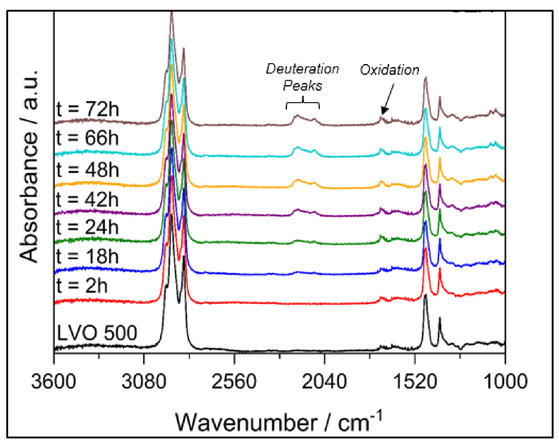
- A mixture of 5g LVO 500 mineral oil and catalyst is stirred in a batch reactor setup and heated up to 240°C under constant Argon purge.
- Gas is switched to D_2 and aliquots taken with a syringe at time intervals for FTIR measurements.
- Each reactor mixture was normalized to 1wt% catalyst loading unless otherwise stated.

Results

XRD

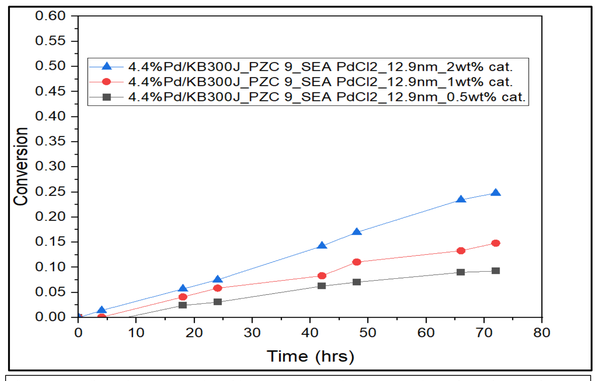


FTIR



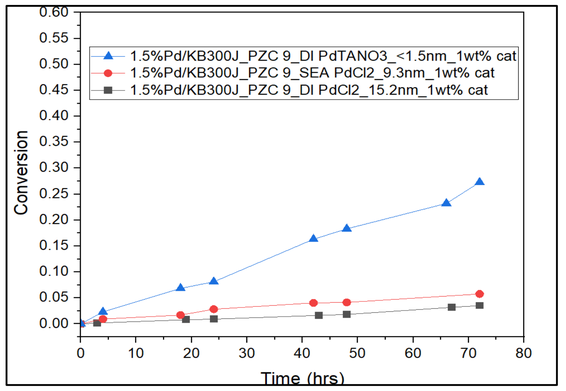
Reaction Data

Catalyst Loading Effect

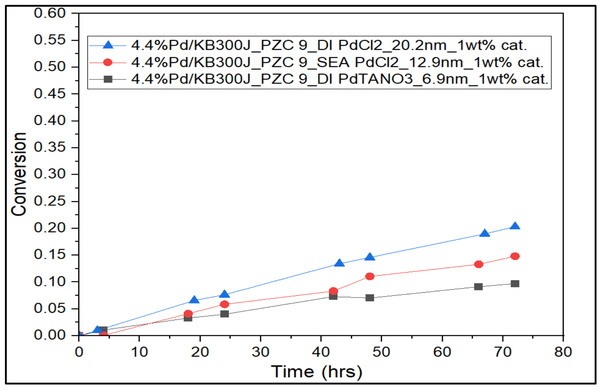


- There is a proportional increase in protium conversion when the catalyst amount is increased.

Particle Size Effect

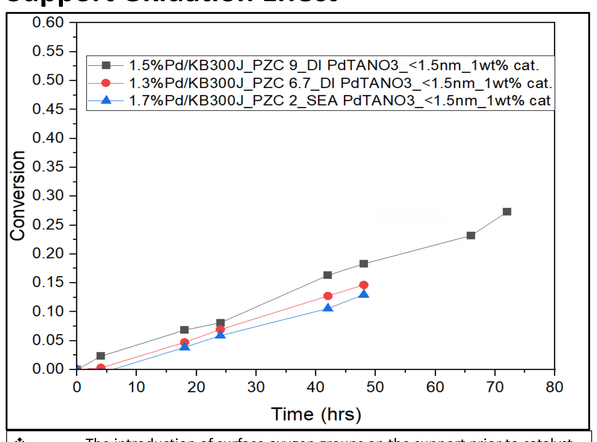


- Small particles performed better.



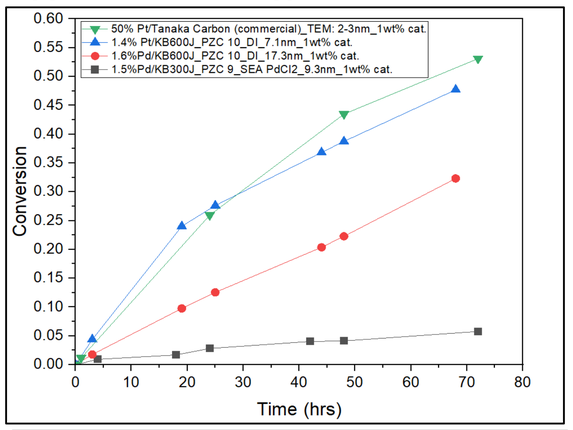
- At higher metal loading, larger particles performed better. .

Support Oxidation Effect



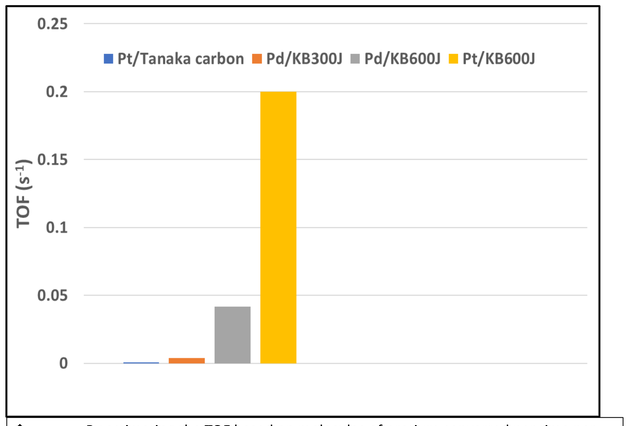
- The introduction of surface oxygen groups on the support prior to catalyst synthesis, had minimal effect on protium conversion to deuterium.

Support and Metal type Effect



- Pt particles appear to be more active than Pd

TOF comparison



- By estimating the TOF based on molecules of protium converted per time per surface Pt atom calculated from XRD size, Pt/KB600J performed several times better than the commercial Pt catalyst and even Pd/KB600J.

Conclusion/ Next Steps

- SEA particles made using the robust palladium tetrammine nitrate ($PdTANO_3$) precursor gave small sizes, as against those made using $PdCl_2$ precursor stabilized in HCl. The diffraction pattern showing prominent Pd peaks corresponds to large metal size while broader peaks corresponds to more dispersed particles.
- The peak at 2130cm^{-1} and 2070cm^{-1} wavenumber of the FTIR plots corresponds to deuterium and was shown to increase in area, with increase in reaction time.
- As expected, higher conversion of the protium in the LVO 500 mineral oil is observed as catalyst loading increased from 0.5wt% to 2wt%.
- Small particles at low Pd loading (1.5%) were more active for deuteration while large particles were more active at high Pd loading (4.4%)
- Surface oxidation had minimal effect on oil deuteration.
- Pd catalyst supported on KB600J was more active than that on KB300J perhaps due to the difference in porosity of the supports.
- Pt/KB600J was far more active than commercially available Pt/Tanaka carbon, confirming again, support effect on deuteration.
- Our next plan is to study the most active catalysts in microwave reactors with anticipated improved performance due to better control of catalyst heating. Also, different forms of supports such as activated carbon, graphitic carbon will be compared to the performance of the best performing ketjen black supports explored so far.

References

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