Hydrothermally Stable Ti-PMO Catalysts for Sustainable Aviation Fuel Synthesis

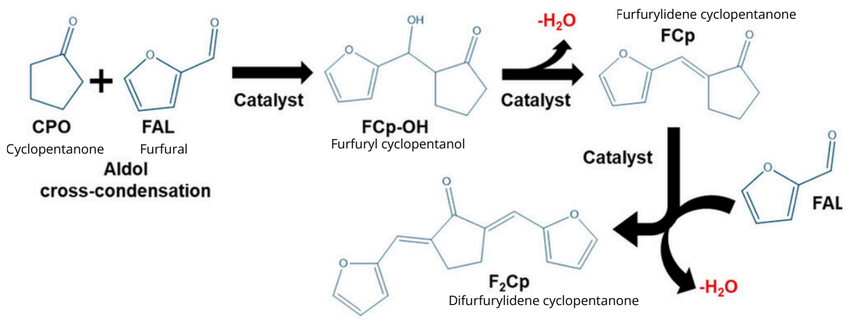
Niyathi Srinivasan,[1,2,3] Lucy Costley-Wood,[1,3] Lee Durndell,[4] Vannia dos-Santos Durndell,[4] Mark Isaacs[1,2]

niyathi.srinivasan.25@ucl.ac.uk

1. Department of Chemistry, University College London, London, WC1H 0AJ
2. HarwellXPS, Research Complex at Harwell, Harwell Campus, OX11 0FA
3. UK Catalysis Hub, Research Complex at Harwell, Harwell Campus, OX11 0FA
4. School of Geography, Earth and Environmental Sciences, Faculty of Science and Engineering, Plymouth University, Plymouth, PL4 8AA UK

Introduction

- Sustainable aviation fuel (SAF) production requires efficient heterogeneous catalysts to convert biomass-derived platform molecules into fuel precursors
- What is Ti-grafted SBA-15 used for?
  - Used in the Lewis acid-catalyzed double aldol condensation of cyclopentanone and furfural, a key step in SAF synthesis
  - Also photolytically enhanced, pointing to a photocatalytic role for the Ti sites alongside their Lewis acid activity
  - But, generates water as a by-product, which can accelerate catalyst degradation and reduce long-term performance.



- How can periodic mesoporous organosilicas (PMOs) help?
  - Incorporate organic bridges directly into the silica framework, increasing hydrophobicity and hydrothermal stability.
  - May also promote improved charge separation through their aromatic framework, offering potential benefits for photocatalytically active Ti sites.
- Solution:
  - Combining Ti active sites with a hydrophobic PMO support may therefore produce catalysts that maintain activity while exhibiting greater stability under hydrothermal reaction conditions.

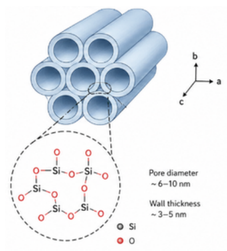
Aims

To combine the photocatalytic activity of Ti-grafted SBA-15 with the hydrothermal stability of PMO supports.

Objective 1: Determine whether PMOs exhibit greater hydrothermal stability than SBA-15 (industry standard)
Objective 2: Synthesize Ti-PMO and evaluate its photocatalytic properties

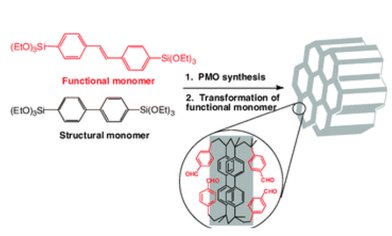
Materials

SBA-15



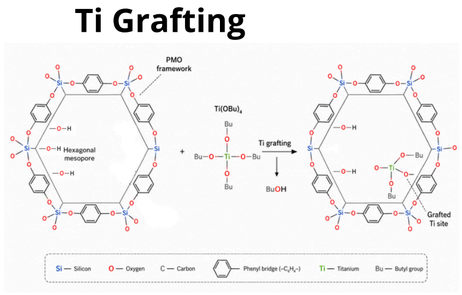
- Surface silanol groups enable Ti grafting
- Made by taking a surfactant like P123, assembling the template, adding a silica precursor (TEOS), and extracting/calcining the template

100% BTSB PMO



- Organic phenylene bridges incorporated into pore walls
- Increased hydrophobicity and hydrothermal stability
- π-electron interactions

Ti Grafting

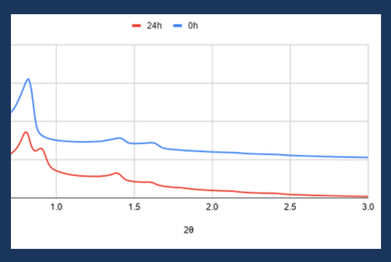


- Isolated Ti(IV) Lewis acid sites
- Surface grafting preserves pore structure
- Produces photocatalytically active Ti centres

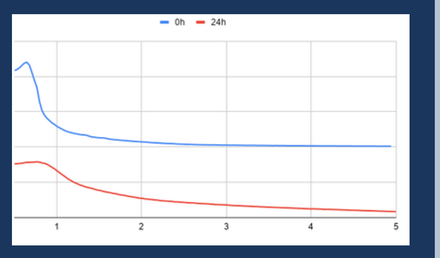
Objective 1: Does the PMO have better hydrothermal stability?

Yes!

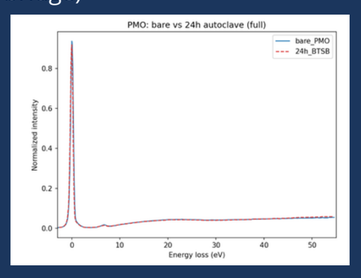
SBA-15 0h vs. 24h

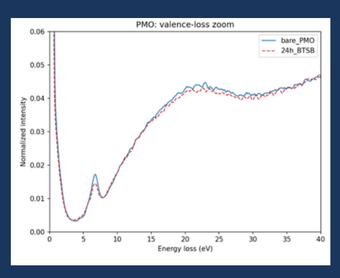


100% BTSB PMO 0h vs. 24h



- SBA-15 loses higher-order peaks
  - (110) and (200) peaks can only appear if the (100) planes are repeated with long-range hexagonal periodicity
  - So, 24h of hydrothermal treatment destroys long-range order, even though short-range order survives (split (100) peak)
- 100% BTSB PMO retains periodic order after 24h (due to aromatic bridge)



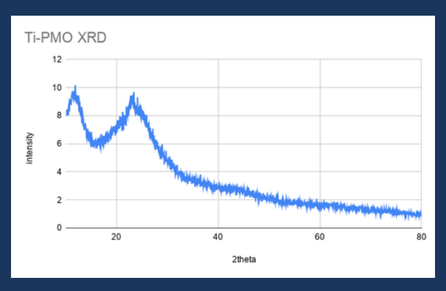


REELS show no shift in electronic structure post-treatment for the PMO

Objective 2: Has the new Ti-PMO been successfully synthesized?

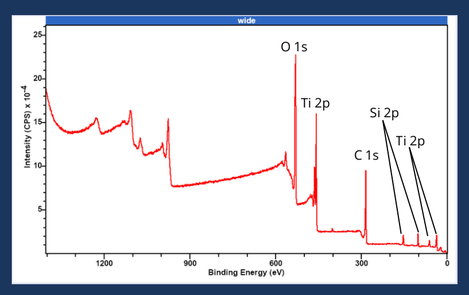
Yes!

Wide-Angle XRD:

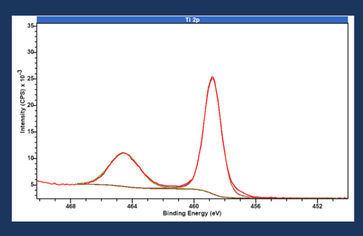


- Broad peak at 8-12° 2θ: low angle reflection of a PMO (shows ordered mesopore structure)
- Broad peak at 23° 2θ: amorphous silica from short range Si-O-Si order
- No sharp peaks anywhere from 25-80° (i.e., no anatase or rutile TiO2)

XPS:

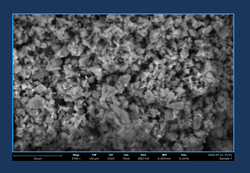


- Ti, O, Si, and C are all present on the surface
- The Ti 2p 3/2 peak is higher than in TiO2, around 459-459.5 (Si-O-Ti environment is more electron withdrawing than Ti-O-Ti)

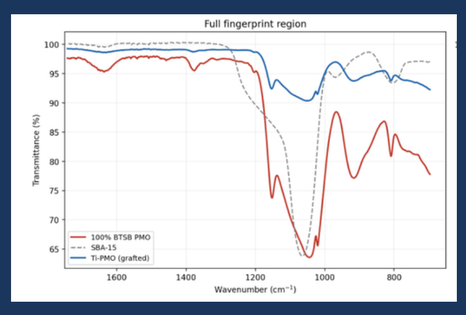


- Ti 2p3/2 and Ti 2p1/2 are separated by ~5.7 eV and the 2p 1/2 peak is half the intensity of 2p 3/2
- There is no Ti(III) shoulder (so the material is fully oxidized Ti(IV)

SEM image of the grafted Ti-PMO

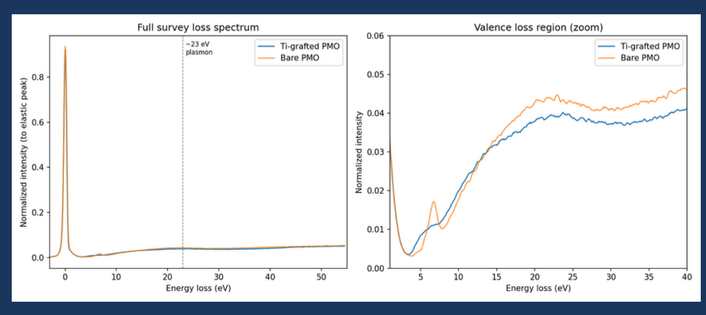


FTIR:



Shared aromatic C–H bending bands in BTSB-PMO and Ti-PMO.
So, the phenylene bridge was retained after Ti grafting (bands are absent in SBA-15).

REELS:



Both samples show an elastic peak at 1004.5–1004.6 eV kinetic energy and a dominant valence-loss feature at ~23 eV.
So, the surface electronic structure of PMO is unaffected by Ti grafting.

Conclusion & Future Work

- Ti-PMO retains long-range order after 24h hydrothermal treatment (unlike Ti-SBA15) and shows 2.4x higher intrinsic per-site photocatalytic activity despite 2.5x lower Ti loading
- Catalyst hydrothermal stability directly limits SAF production: a support that is hydrothermally stable means longer catalyst lifetime and lower cost per litre of fuel produced at scale

N_2 physisorption (BET)

To quantify surface area, pore diameter and pore volume before and after hydrothermal ageing.

Photoluminescence spectroscopy

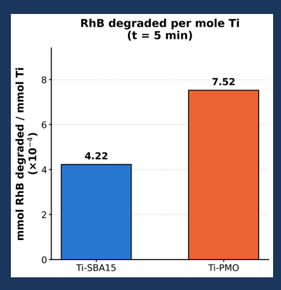
To investigate charge-carrier separation and electronic coupling between Ti centres and the aromatic PMO framework.

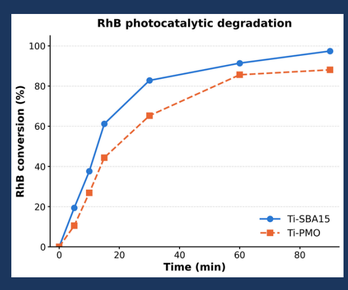
Catalyst Durability

To assess catalyst lifetime through repeated reaction cycles and determine long-term stability under realistic operating conditions

Photocatalytic Performance: RhB Degradation

Conditions: 20 mg catalyst, 20 mL of 8 mg/L RhB solution.





Ti-PMO degrades 1.78x more RhB per mole Ti than Ti-SBA15 despite having 2.5x less Ti loading, indicating higher intrinsic activity per Ti site. Ti-SBA15 reaches near-complete conversion (97.4%) faster than Ti-PMO (88.1% at 90 min), reflecting its higher total Ti loading.

EDX:

Material	% Ti	Initial Rate (mg/L·min)	Initial TOF (min^{-1})	Overall TOF (min^{-1})
Ti-SBA	9.75	0.084	0.086	0.023
Ti-PMO	3.96	0.083	0.210	0.069

- Ti-PMO's per-site TOF is roughly 2.4x higher than Ti-SBA15's
- The two catalysts degrade RhB at nearly identical raw rates early on (0.084 vs 0.083 mg/L·min), but Ti-PMO does it with less than half the Ti content

References & Acknowledgements

- Isaacs, M. A.; Drivas, C.; Graf, A.; et al. Understanding the Chemical and Electronic Properties of Sub-Monolayer TiO_2 on High Surface Area Silica for Jet Fuel Synthesis Applications. Adv. Funct. Mater. 2025, 36, e02818. https://doi.org/10.1002/adfm.202502818.
- dos Santos-Durndell, V. C.; Isaacs, M. A.; Manayil, J. C.; et al. Light or Acid? Suppressing Water Deactivation in SAF Production via Phenyl-Mediated Charge Transfer in WOx/ZrOx-Functionalised PMOs. Appl. Catal. O: Open 2025, 209, 207078. https://doi.org/10.1016/j.apcato.2025.207078.
- dos Santos-Durndell, V. C.; Durndell, L. J.; Isaacs, M. A.; Lee, A. F.; Wilson, K. WOx/ZrOx Functionalised Periodic Mesoporous Organosilicas as Water-Tolerant Catalysts for Carboxylic Acid Esterification. Sustainable Energy Fuels 2023, 7, 1677–1686. https://doi.org/10.1039/D2SE01724E

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