Catalytic Processes for Sustainable Chemicals and Fuels

Professor Sir Richard Catlow FRS
Department of Chemistry, University College London, Royal Society,
United Kingdom

Materials Design UGM

UGM 2021

The Materials Design annual user event will be online again for 2021.

Plenary Speakers include:

Prof. Michele Parrinello
Prof. Georg Kresse
Prof. Richard Catlow

materials design

Email

SEND ME UPDATES

https://ugm.materialsdesign.com/

Catalytic Processes for Sustainable Chemicals and Fuels

Professor Sir Richard Catlow FRS
Department of Chemistry, University College London, Royal Society,
United Kingdom

Materials Design UGM Presenter

Professor Sir Richard Catlow FRS

University College London

Plenary Session Speakers

Katherine Hollingsworth

khollingsworth@materialsdesign.com

Dr. Clive Freeman

cfreeman@materialsdesign.com

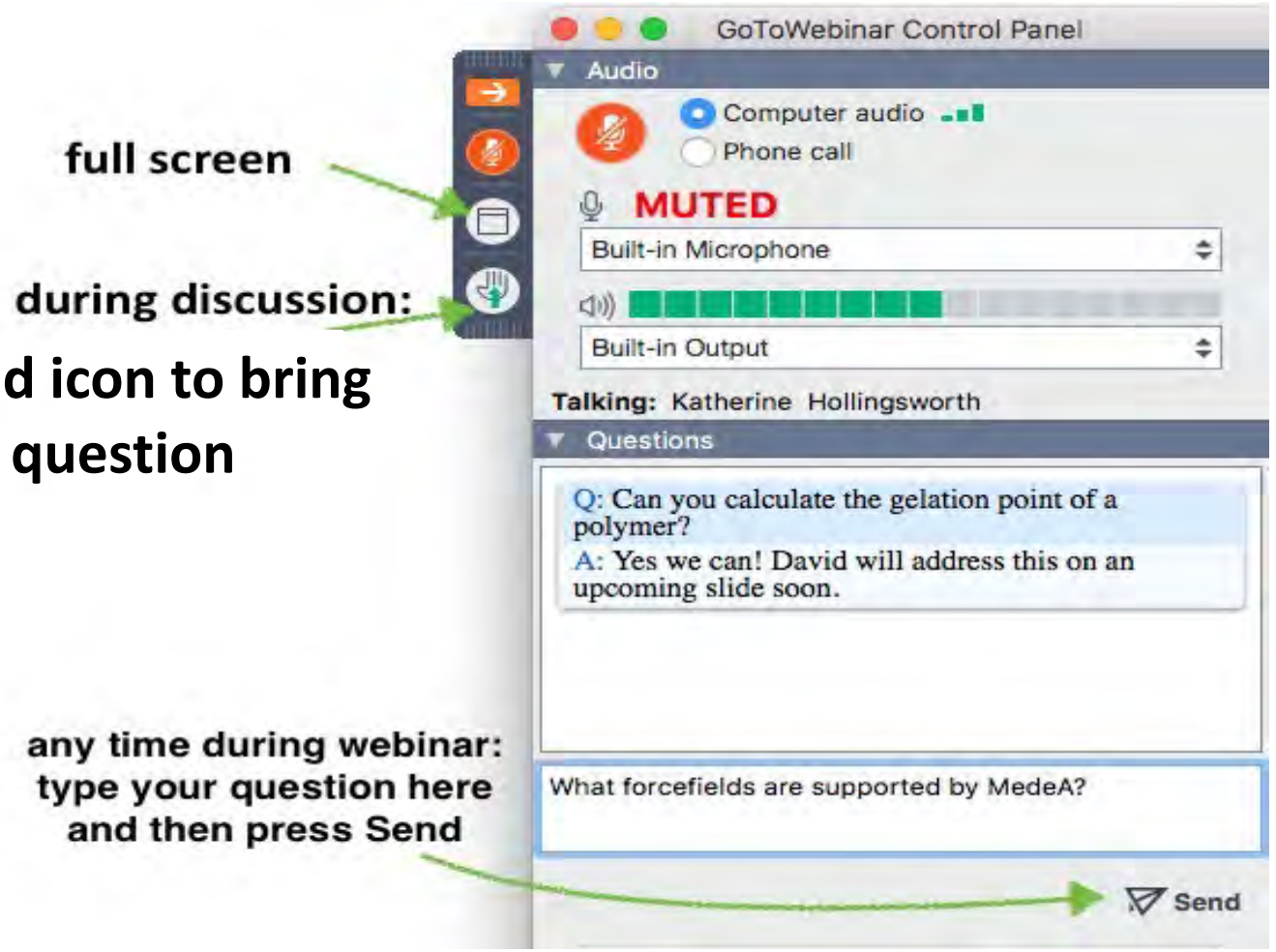
Materials Design UGM Plenary Sessions

- Share the plenary sessions with your colleagues!
  - Registration details

    https://www.ugm.materialsdesign.com
- We will be recording this session
  - Upcoming sessions are posted on the UGM site
  - Watch any of our earlier webinars anytime www.materialsdesign.com/webinars
- Brief survey
  - Take a 2 minutes brief survey at the end of the webinar
- Audio issues
  - Log out and log back in again
  - Check your audio output
  - Google Chrome (most recent 2 versions) Mozilla Firefox (most recent 2 versions) Apple Safari (most recent 2 versions) Microsoft Edge (most recent 2 versions)

Please Ask Questions!

Use the raise hand icon to bring attention to your question



Catalytic Processes for Sustainable Chemicals and Fuels

Professor Sir Richard Catlow FRS
Department of Chemistry, University College London, Royal Society,
United Kingdom

CATALYSIS for SUSTAINABLE CHEMICALS and FUELS:

Richard Catlow
Cardiff Catalysis Institute,
School of Chemistry,
Cardiff University;
Dept of Chemistry,
University College London;
UK Catalysis Hub,
Research Complex at Harwell

CatalysisHub

CARDIFF UNIVERSITY
PRIFYSGOL CAERDYDD

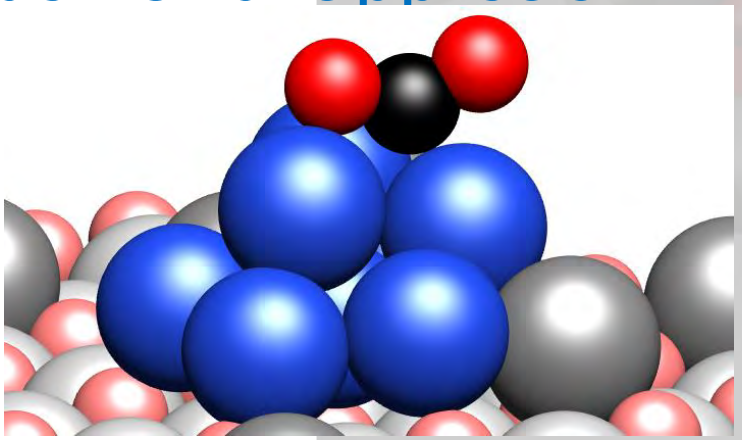
UCL

THEME:

Catalysis is a core process in the Fuels and Chemicals Industry

Understanding and optimising catalytic chemistry is vital for sustainable processes

Modelling in combination with experiment provides a powerful approach



CARDIFF UNIVERSITY
PRIFYSGOL CAERDYDD

UCL

SYSTEMS:

C1 Chemistry

- *CO/CO_2 hydrogenation to methanol*
- *Methanol to gasoline*
- (Fisher Tropsch (CO/H_2 to hydrocarbons)

Dynamics of Sorbed Molecules in Microporous Materials

Ammonia Synthesis

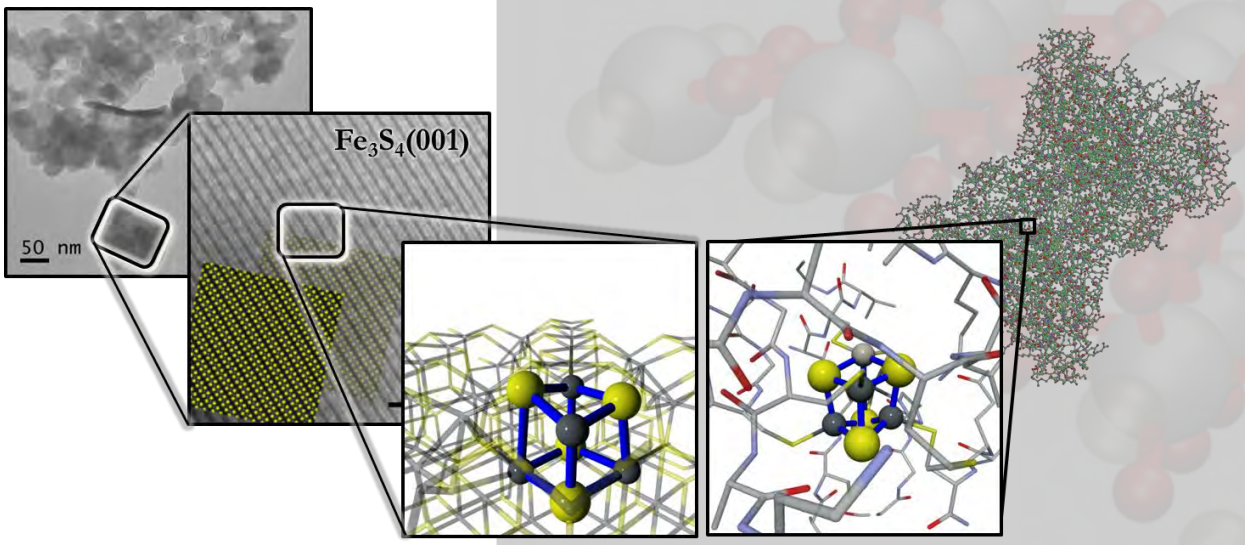
Insight and optimisation of key catalytic processes using modelling and experiment

CARDIFF UNIVERSITY
PRIFYSGOL CAERDYDD

UCL

THEME ONE:
CO/CO2 Hydrogenation

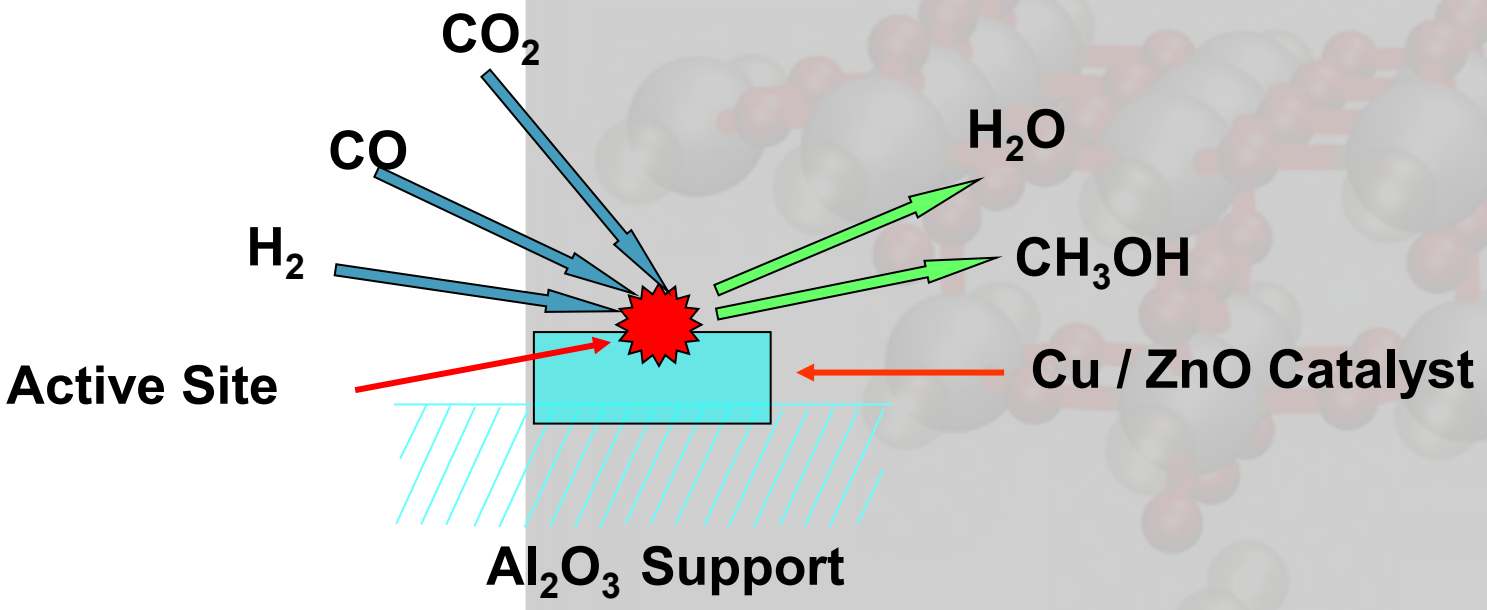
- Cu/ZnO catalysis for methanol synthesis
- Iron Sulfides as Hydrogenation Catalysts
- Methanol to Gasoline



METHANOL SYNTHESIS

- **BASF 1923** high pressure catalyst 300 bar, < 300 °C
  Zinc Oxide / Chromia

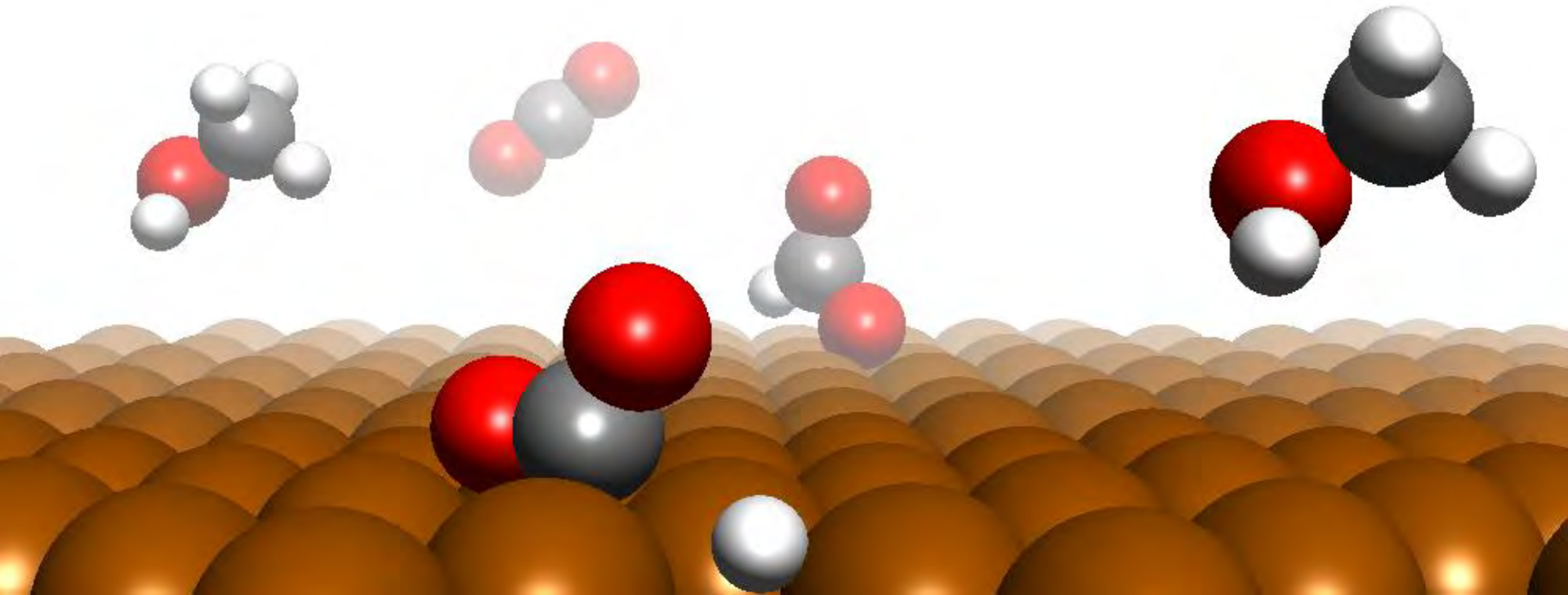
- **ICI 1965** low pressure catalyst 40-110 bar, 200–300 °C
  Copper / Zinc Oxide / Alumina



Mechanism of CO_2 Conversion to Methanol over Cu(110) and Cu(100)

Michael Higham

Higham and Catlow
Dalton Trans., 2020,**49**, 8478-8497



Background

- Methanol is an attractive target molecule for CO_2 – major industrial chemical, potentially a renewable feedstock material for synthetic hydrocarbons, also a potential candidate material as a stable hydrogen source for hydrogen fuel cells[1] – Direct Methanol Fuel Cells (DMFC)[2].
- $Cu/ZnO/Al_2O_3$ has long been used as a catalyst for methanol synthesis[3].
- Precise role of the ZnO support is not well understood – several potential routes for enhanced activity compared to unsupported Cu, e.g. enhanced Cu surface area[4]; role of ZnO bulk defects[5]; formation of surface ZnO islands facilitating a synergistic mechanism[6] etc.
- Objective: to investigate through computational techniques the mechanism of CO_2 conversion to methanol over low-index Cu surfaces to explore a wide range of reaction pathways, identify key elementary processes, and thus provide a framework for comparison for future studies investigating systems representative of the industrial Cu/ZnO catalyst.

1. J. Org. Chem. 2009, 74, 487
2. Plat. Met. Rev. 1996, 40, 150
3. UK Patent 101087, 1996
4. Appl. Catal. 1986 ,25, 101
5. Top. Catal. 2003, 24, 161
6. Science, 2012, 336, 893

Methodology - Computational Details

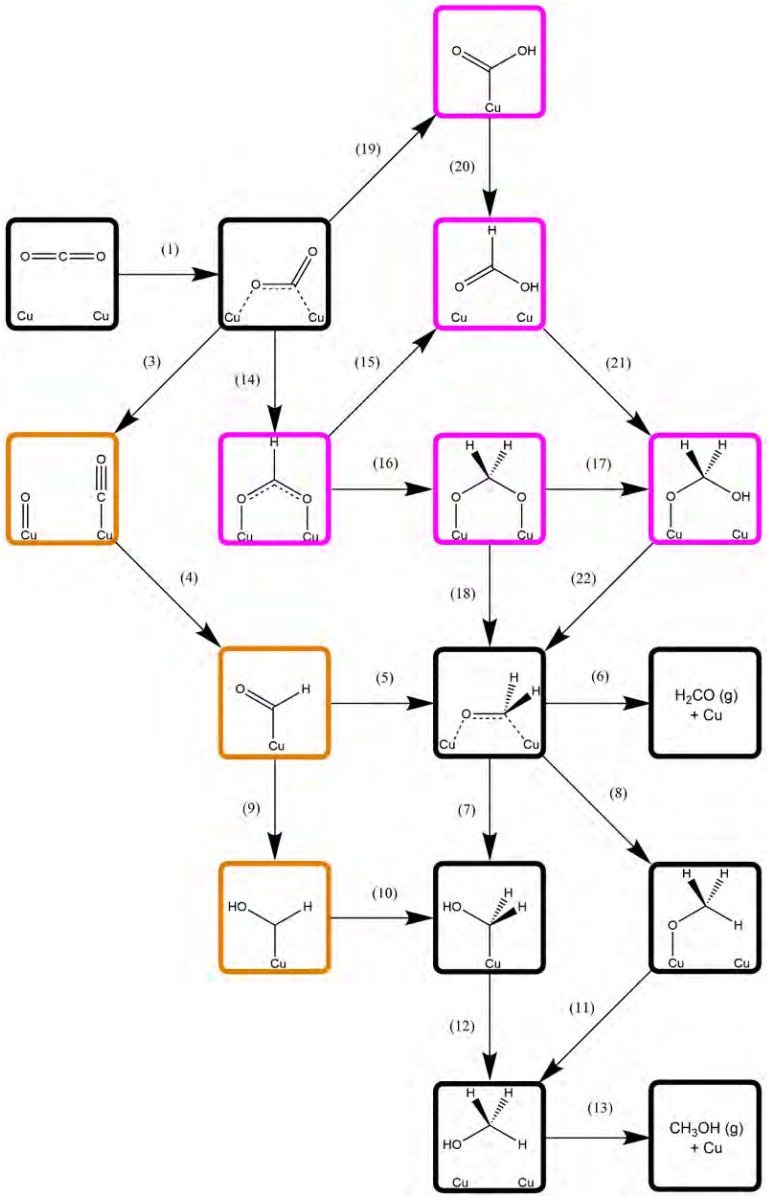
- Periodic DFT: VASP v. 5.4.4[7][8]
- XC functional: PBE-D2[9] – good correspondence with experimental Cu bulk lattice parameter when corrected for thermal expansion and ZPE[10] (*a*=3.57Å, obtained from fitting to Birch-Murnaghan EOS); CO_2 physisorption on Cu typically dominated by weak Van der Waals interactions[11].

.

- Transition states – CI-NEB method[13,14], saddle point confirmed through vibrational analysis.

7. Comp. Mater. Sci. 1996, 6, 25
8. Phys. Rev. B. 1996, 16, 11169
9. J. Comput. Chem. 2006, 27, 1787
10. Phys. Rev. B 2009, 79, 155107
11. J. Catal. 2011, 281, 199
12. Phys. Rev. B 1976, 13, 5188
13. J. Chem. Phys., 2000, 113, 9978.
14. J. Chem. Phys., 1999, 111, 7010–7022.

Reaction Map



$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

- Several different mechanistic pathways to methanol formation are investigated.
- H_2 adsorption and dissociation and H_2O formation common to all pathways.
- CO_2 dissociation followed by CO hydrogenation vs. direct CO_2 hydrogenation.
- Formate (HCOO*) vs. hydrocarboxyl (COOH*) formation.
- Formic acid (HCOOH*) vs. dioxomethylene (OCH_2O*).
- Fomaldehyde – common intermediate to several different pathways.
- Methoxy (CH_3O*) vs. hydroxymethylene (CH_2OH*).
- Competitive adsorption between CO_2, intermediatates HCOOH and H_2CO, and product CH_3OH.

CO_2 Adsorption and Activation

- CO_2 physisorption observed for all three low-index Cu surfaces: (111), (110), (100).

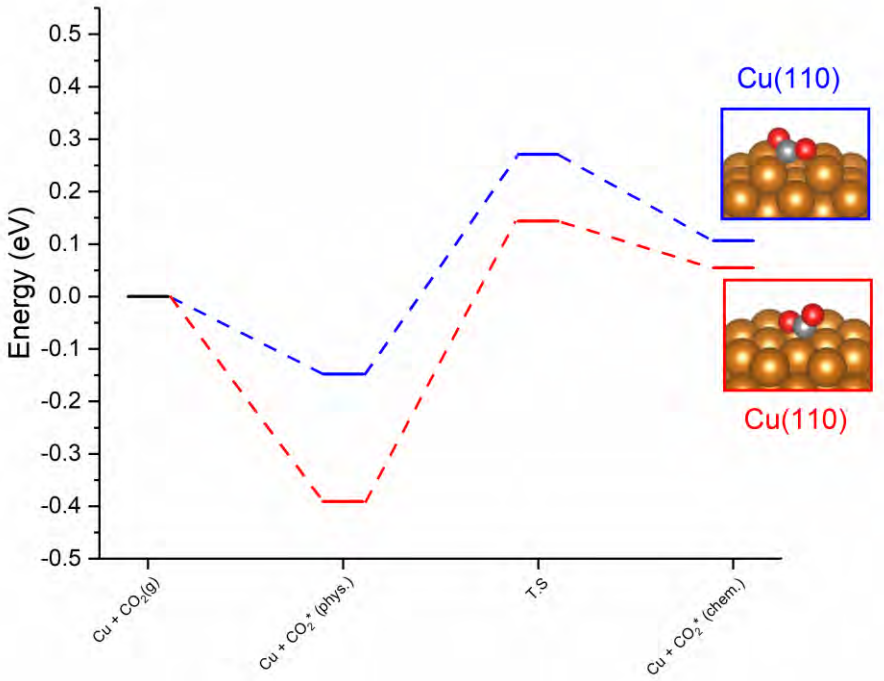
Cu facet	$E_{ads.}$ / eV	$d_{(Cu-C)}$ / Å	$d_{(C-O)}$ / Å	∠ (O-C-O) / °
(111)	-0.353	3.41	1.18	179.45
(110)	-0.148	3.49	1.18	179.40
(100)	-0.391	3.43	1.18	179.20

- Second bent "chemisorbed" CO_2 species observed for Cu(110) and Cu(100) – but not Cu(111).

Cu facet	ΔE / eV	E_a / eV	v / cm^{-1}	$d_{(Cu-C)}$ / Å	$d_{(C-O)}$ / Å	∠ (O-C-O) / °
(110)	0.254	0.419	190.97	1.998	1.27, 1.27	127.53
(100)	0.446	0.535	181.67	2.141	1.22, 1.33	128.45

- Bent CO_2 is less stable than linear physisobed species and gas phase CO_2 – metastable intermediate.
- Changes in CO_2 adsorption geometry imply transfer of electrons from Cu to CO_2 i.e. CO_2 activation.

CO_2 Adsorption and Activation

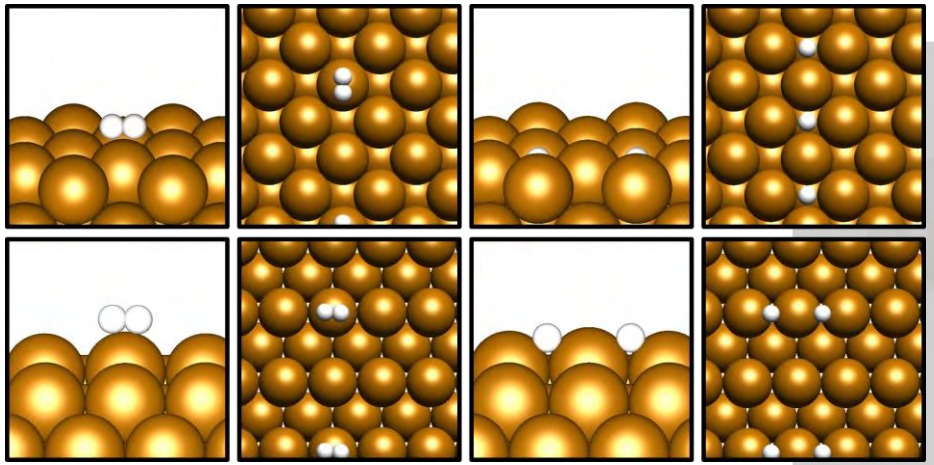


- Bader charge analysis shows moderate extent of electron transfer to CO_2 – $\Delta\beta \approx 0.7e$ for both Cu(110) and Cu(100) – c.f. $1.2 < \Delta\beta < 1.8$ for TM carbides[15].
- Activation barriers for transition from physisorbed to chemisorbed moderate.
- Chemisorbed CO_2 is likely a short-lived species – but could be relevant if it undergoes further elementary processes (i.e. dissociation, hydrogenation) which are irreversible.
- Observed order of CO_2 adsorption activity consistent with previous studies – (111) < (100) < (110)[16-19].
- Cu(110) and Cu(100) selected for further investigation for hydrogenation.

15. Phys. Chem. Chem. Phys., 2019, 21, 10750–10760.
16. J. Catal., 1996, 161, 776–782.
17. Surf. Sci., 1979, 83, 45–59.
18. Surf. Sci., 2004, 570, 205–217.
19. J. Chem. Phys., 2004, 121, 4339–45.

H_2 Adsorption and Dissociation

- H_2 dissociative adsorption – key prerequisite for MeOH formation.
- H_2 weakly physisorbs exothermically atop Cu atoms – dissociation to 2H* exothermic by ~0.2 eV.
- Modest to moderate activation barrier for H_2 dissociation – 0.28 eV for Cu(110), 0.52 eV for Cu(100).
- Consistent with previous experimental work on H_2 behaviour over Cu surfaces.



Cu facet	$E_{ads.}$ (phys.) / eV	$\Delta E_{diss.}$ / eV	E_a / eV	v / cm^{-1}
(110)	-0.113	-0.210	0.284	811.542
(100)	-0.083	-0.197	0.517	1239.385

18. Surf. Sci., 1989, 220, 1–17.
19. J. Chem. Phys., 1995, 102, 3873–3883.
20. J. Chem. Phys., 1994, 100, 5956–5964.
21. Chem. Phys. Lett., 1993, 213, 422–426.

CO_2 Dissociation

- $CO_2^* + * \rightarrow CO^* + O^*$
- Moderate activation barrier of 0.7 – 0.8 eV.
- Slightly exothermic for Cu(100), endothermic for Cu(110).
- Experimental evidence for CO_2 dissociation over Cu surfaces[22-24], but the calculations suggest that the process is likely to be uncompetitive compared to e.g. CO_2 hydrogenation.
- Possibility of CO as an intermediate for MeOH synthesis warrants further investigation.

Cu facet	ΔE / eV	E_a / eV	V / cm^{-1}	$d_{(C-O)}$ (TS) / Å
(110)	0.520	0.792	182.416	2.032
(100)	-0.083	0.711	319.611	1.943

22. Surf. Sci., 1992, 272, 211–219.
23. Surf. Sci., 1993, 287–288, 104–109.
24. Phys. Chem. Chem. Phys., 1999, 1, 4105–4112.

CO Hydrogenation – Cu(110)

Process No.	Elementary Process	ΔE / eV	E_a / eV	v / cm^{-1}
HCO* Formation				
4	CO* + H* → HCO*	+0.660	1.076	1044.590
H_2CO Formation, Desorption and Hydrogenation				
5	HCO* + H* → H_2CO*	-0.597	0.109	644.746
6	H_2CO* → H_2CO(g)	+0.986	-	-
7	H_2CO* + H* → CH_2OH*	+0.087	0.963	927.927
8	H_2CO* + H* → CH_3O*	-0.622	0.388	328.280
HCOH Formation and Hydrogenation				
9	HCO* + H* → HCOH*	-0.095	0.496	1164.784
10	HCOH* + H* → CH_2OH*	-0.339	0.284	818.827
CH_3OH Formation and Desorption				
11	CH_3O* + H* → CH_3OH*	-0.004	0.960	926.043
12	CH_2OH* + H* → CH_3OH*	-0.705	0.604	610.080
13	CH_3OH* → CH_3OH(g)	+0.771	-	-

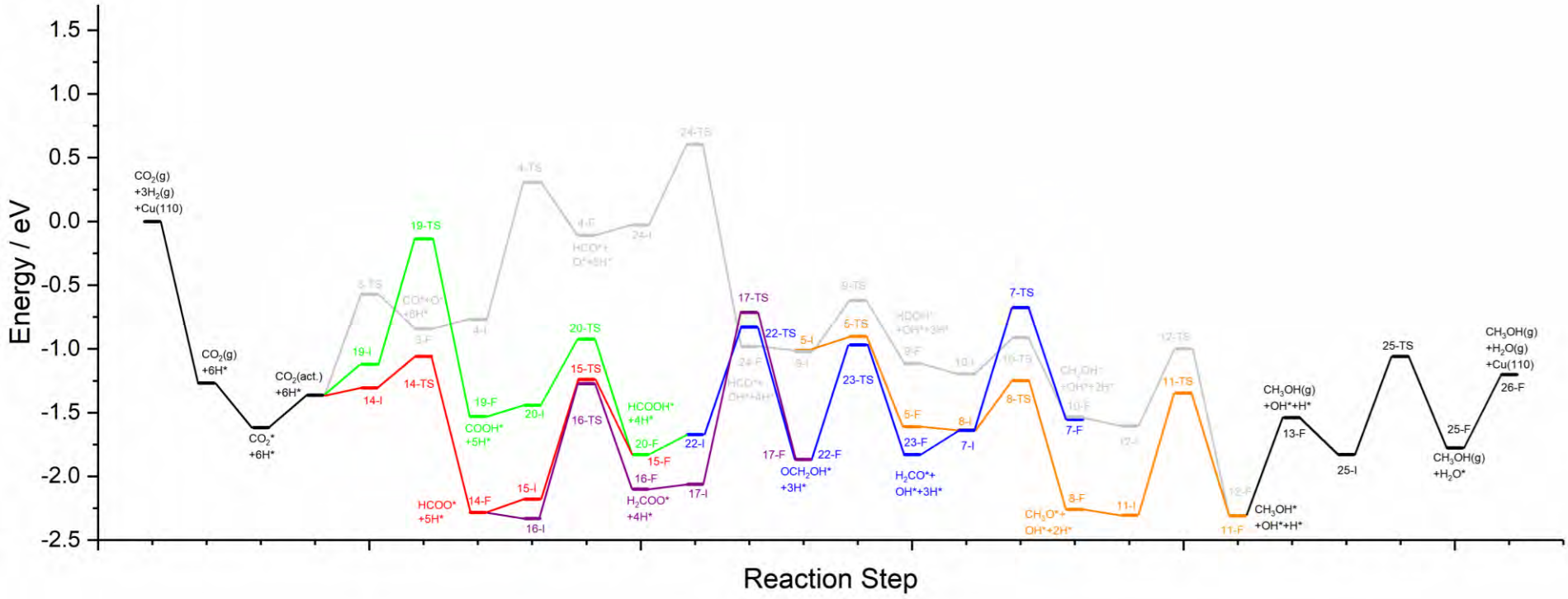
- Initial CO hydrogenation – high barrier and endothermic.
- Formaldehyde formation has a low barrier and is exothermic, but subsequent hydrogenation to CH_3O* and especially CH_2OH much less energetically feasible (although less so than formaldehyde desorption).
- Methanol formation from CH_3O* has a higher barrier than for CH_2OH* - but overall less energetically demanding due to lower barrier for CH_3O* formation.

CO_2 Hydrogenation – Cu(110)

Process No.	Elementary Process	ΔE / eV	E_a / eV	ν / cm^{-1}
HCOO*				
14	CO_2* + H* → HCOO*	-0.978	0.246	702.298
15	HCOO* + H* → HCOOH*	+0.349	0.938	1061.697
16a	HCOO* + H* → H_2COO* (LB)	+0.230	1.056	877.380
17a	H_2COO* + H* → OCH_2OH* (LB)	+0.196	1.348	1146.997
18a	H_2COO* → H_2CO* + O* (LB)	+1.205	1.662	151.468
16b	HCOO* + H* → H_2COO* (SB)	+0.668	1.789	822.753
17b	H_2COO* + H* → OCH_2OH* (SB)	-0.286	0.623	1041.733
COOH*				
19	CO_2* + H* → COOH*	-0.408	0.986	1261.956
20	COOH* + H* → HCOOH*	-0.387	0.517	709.148
21	HCOOH* → HCOOH(g)	+0.816	-	-
HCOOH* Hydrogenation				
22	HCOOH* + H* → OCH_2OH*	-0.194	0.844	606.191
OCH_2OH* Dissociation, H_2CO Desorption and Hydrogenation				
23	OCH_2OH* → H_2CO* + OH*	+0.037	0.899	136.674
6	H_2CO* → H_2CO(g)	+0.986	-	-
7	H_2CO* + H* → CH_2OH*	+0.087	0.963	927.927
8	H_2CO* + H* → CH_3O*	-0.622	0.388	328.280
11	CH_3O* + H* → CH_3OH*	-0.004	0.960	926.043
12	CH_2OH* + H* → CH_3OH*	-0.705	0.604	610.080

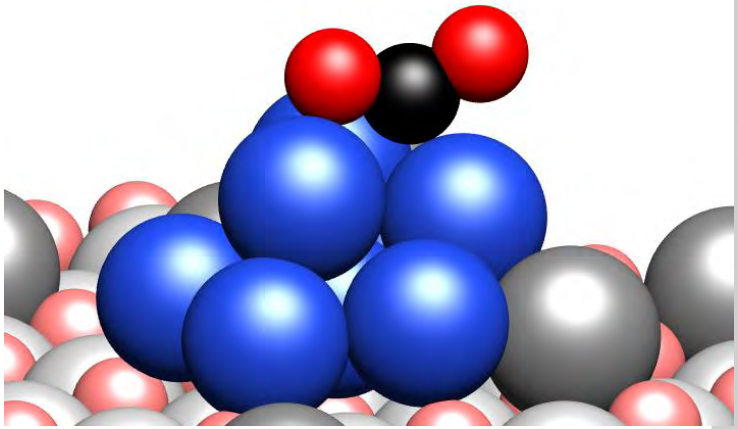
- HCOO* formation less activated that COOH* formation.
- HCOOH* formation from both HCOO* and COOH* is the least activated subsequent process.
- Hence OCH_2OH* formation can be achieved via either HCOO* or COOH* route through HCOOH* hydrogenation – subsequent dissociation to formaldehyde and subsequent processes common with CO pathway.

Reaction Profile – Cu(110)

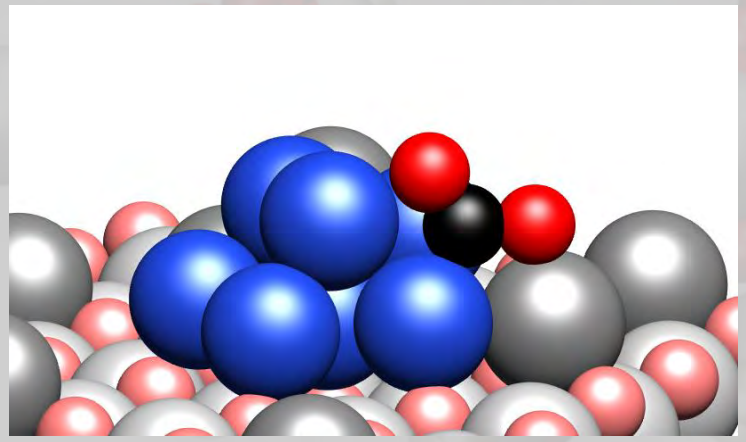


Conclusions and Current/Future Work

- For both Cu(110) and Cu(100), most energetically favourable path for CO_2 hydrogenation appears to be via HCOO*, HCOOH*, OCH_2OH* and H_2CO* - but CH_3O* and CH_2OH are competitive for final hydrogenation to methanol.
- CO hydrogenation route appears to be too activated overall.
- Current work: CO_2 adsorption and activation over model Cu/ZnO catalysts appears to be enhanced – hence possibility for more energetically demanding pathways over unsupported Cu to become viable over supported Cu nanoclusters – visiting student David Jurado.
- Future work will investigate all possible CO_2 conversion pathways over model Cu/ZnO catalysts.



CO_2 on top of Cu cluster
$\Delta\beta = 0.65$, $\Delta E = -0.25$
$\angle$ (O-C-O) = 133.35°



CO_2 at Cu-Zn interfacial site
$\Delta\beta = 0.77$, $\Delta E = -0.23$
$\angle$ (O-C-O) = 123.95°

Iron and Iron-Nickel Catalysts for CO_2 hydrogenation

C.E. Mitchell, D. Santos-Carballal, A.M. Beale, W. Jones, D.J. Morgan, M. Sankar,

Nora H. de Leeuw

CatalysisHub

Aims and Background

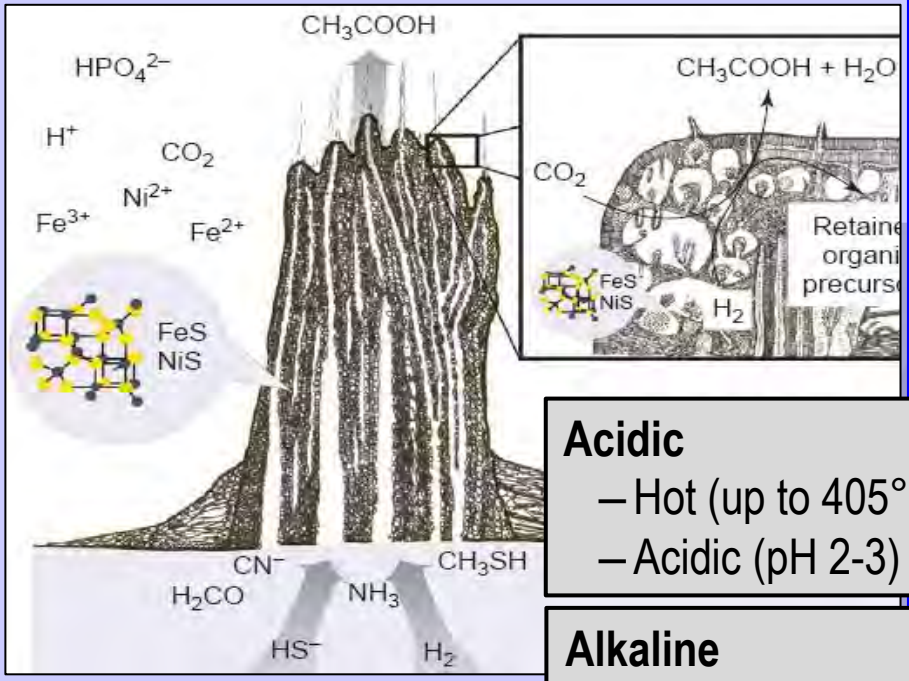
- Aim is again to use CO_2 as C1 carbon source to produce chemical feedstock, e.g. formic acid, methanol, employing catalysts from readily available materials under mild conditions

- Iron and Iron-nickel sulfides show promise:
  - Non-toxic Earth-abundant elements
  - Variable Fe/Ni and S oxidation states – easy electron cycling
  - Active sites in enzymes, e.g. hydrogenases
  - Suggested catalysts in pre-biotic Origin of Life theory

Introduction

Origin of Life

Fe, Ni, Co Sulfides and Silicates



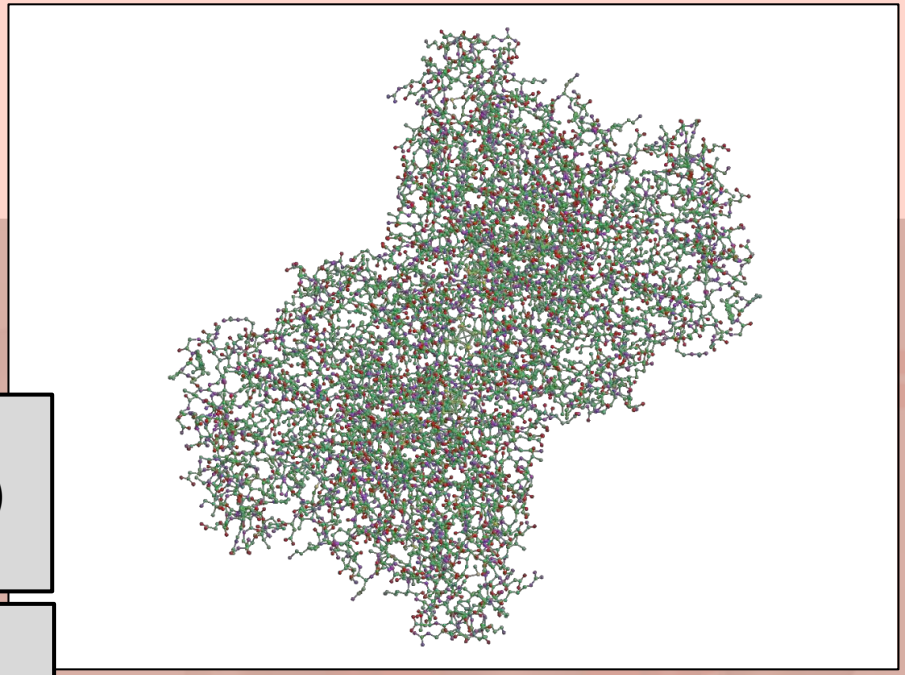
Hydrothermal Vent

Acidic
- Hot (up to 405°C)
- Acidic (pH 2-3)

Alkaline
- Cool (40-90°C)
- Alkaline (pH 10-11)

Capable Enzymes

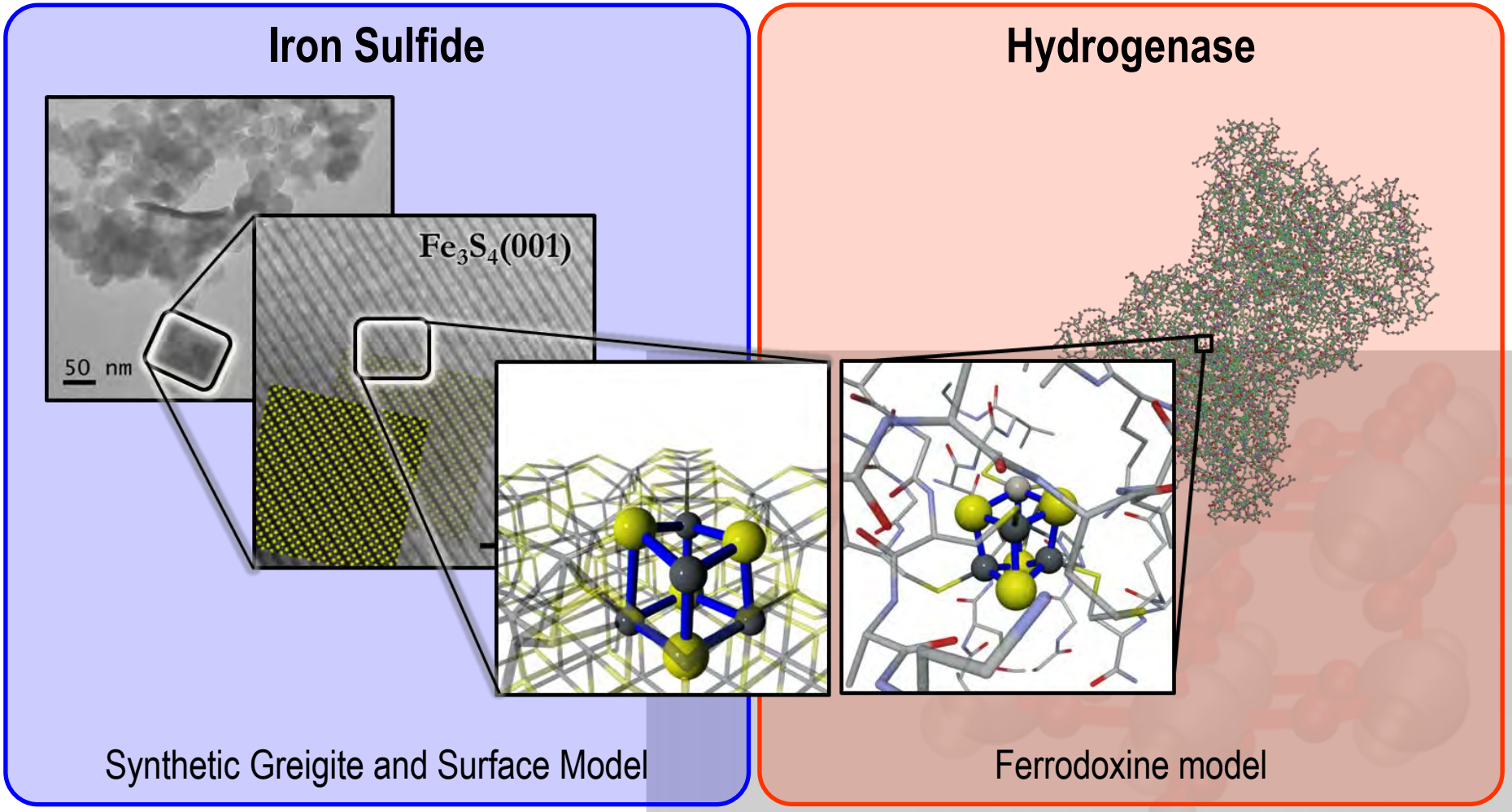
Fe, Ni Sulfide Structure



Biological Hydrogenase

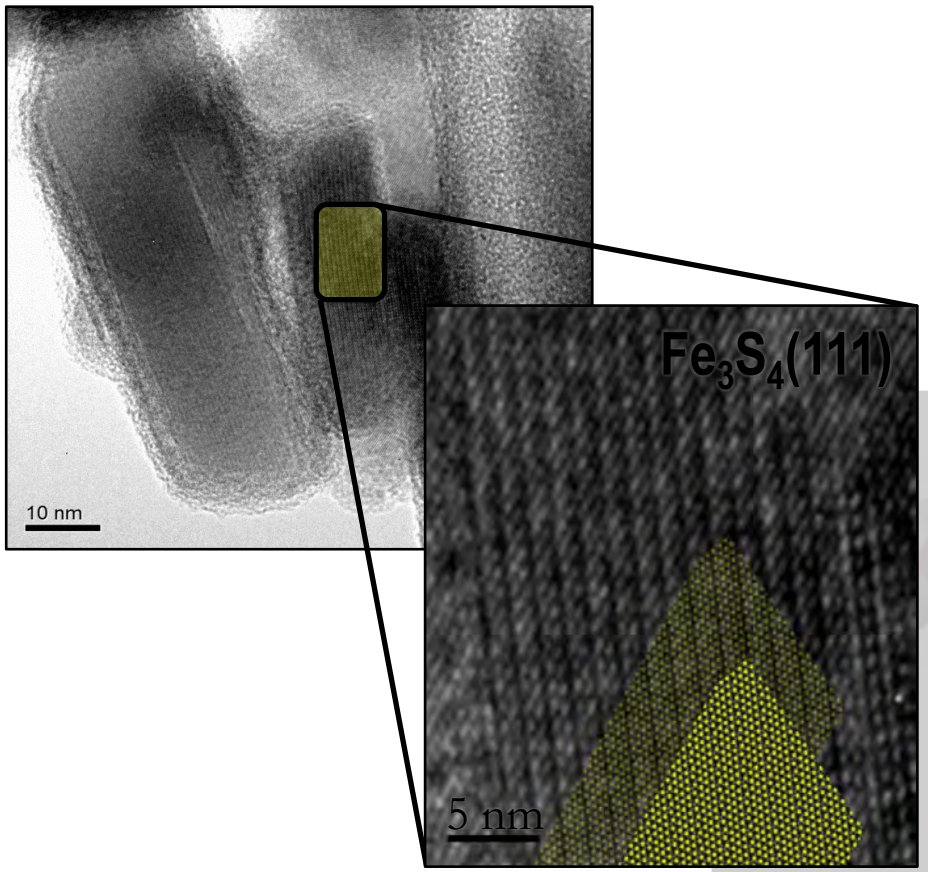
Russell & Martin, *TiBS*, (**2004**) 29, 358; Kelley D. S. et al. *Nature* (**2001**) 412, 145.

Introduction

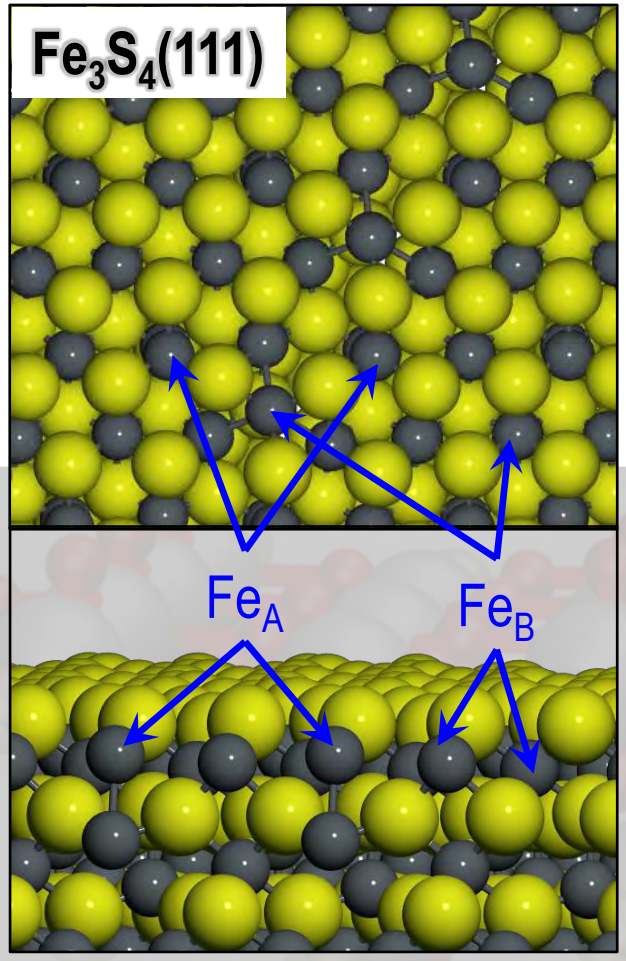


Roldan, *et al.*, *Chem Commun*, (**2015**), 51, 7501

Greigite Surface



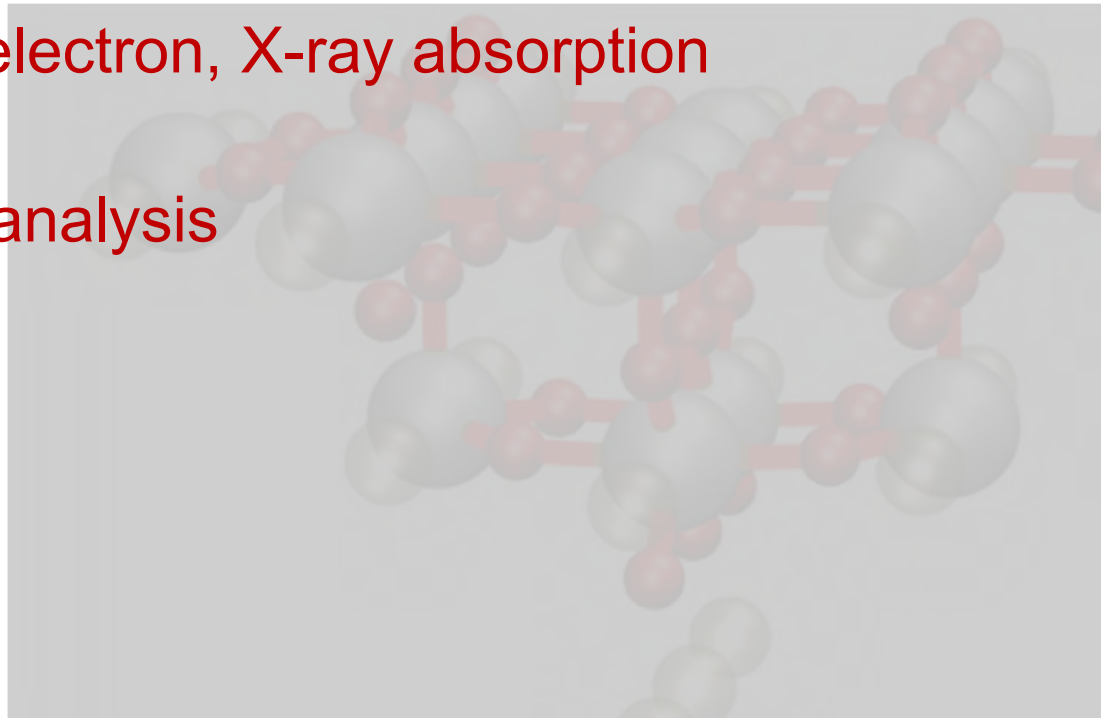
HR-TEM and Model



Top and Side Model view

Experiment

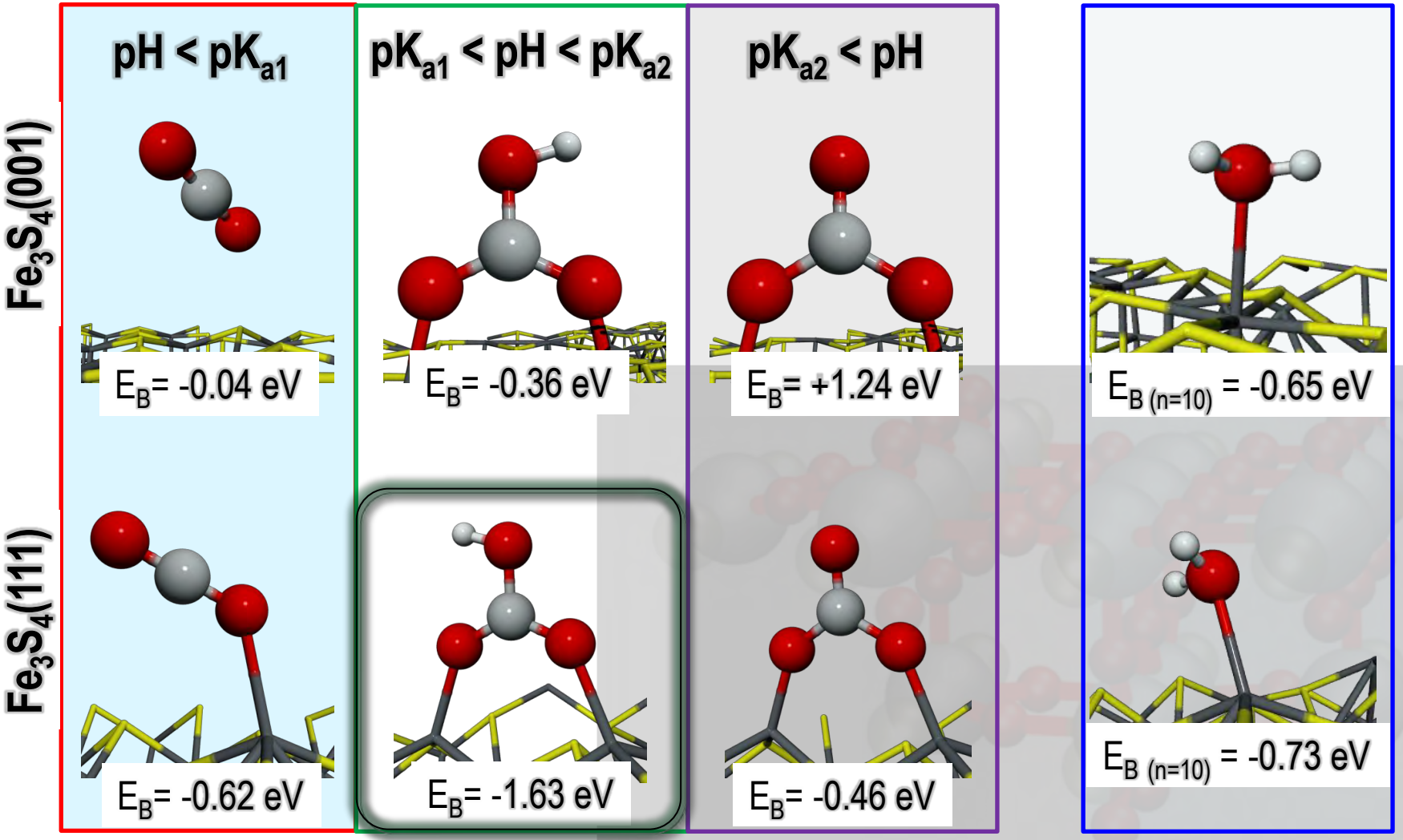
- Multiple characterisation techniques
  - In-situ and powder XRD
  - Raman, X-ray photoelectron, X-ray absorption spectroscopy
  - Thermal gravimetric analysis
  - XAFS and XANES



Computation

- Periodic plane-wave DFT calculations: *meta*-GGA + U + D2 (VASP)
- Semi-local density functional (SCAN)
- U_{eff} (Fe)= 1.7 eV; U_{eff} (Ni)= 2.0 eV)
- Calculation of thermodynamics: Reaction energy between products and reactants
- Calculation of kinetics: Activation energy barriers
- Climbing image NEB method to determine transition states
- Frequency calculations to determine reaction coordinate: 1 imaginary mode

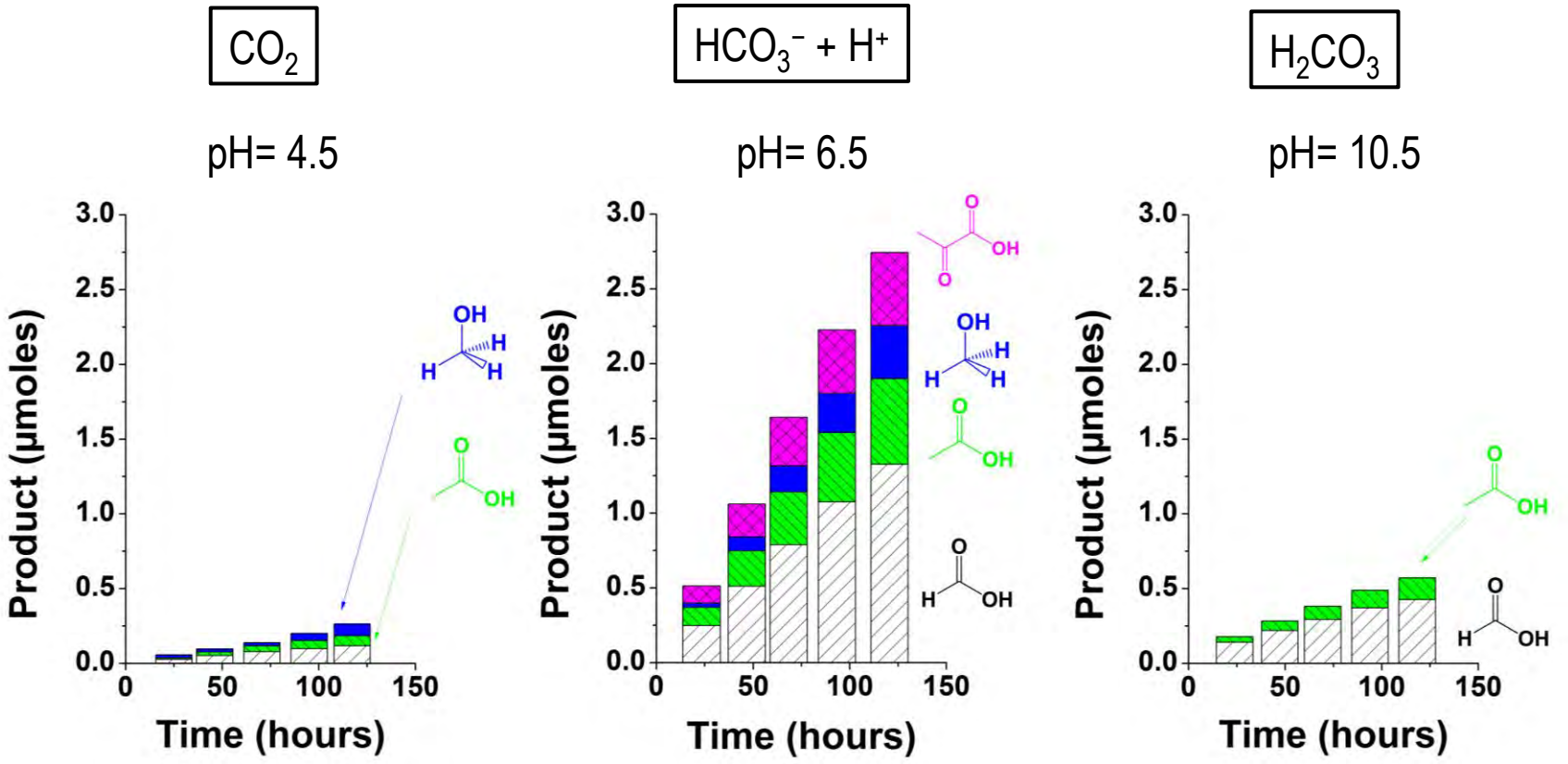
Surface-Solution Interphase



A. Roldan, , N.H deLeeuw *et al. Chem Commun*, **2015**, 51, 7501

Aqueous CO_2 Conversion

- H^1-NMR Quantification



A. Roldan, N.H de Leeuw *et al. Chem Commun*, **2015**, 51, 7501

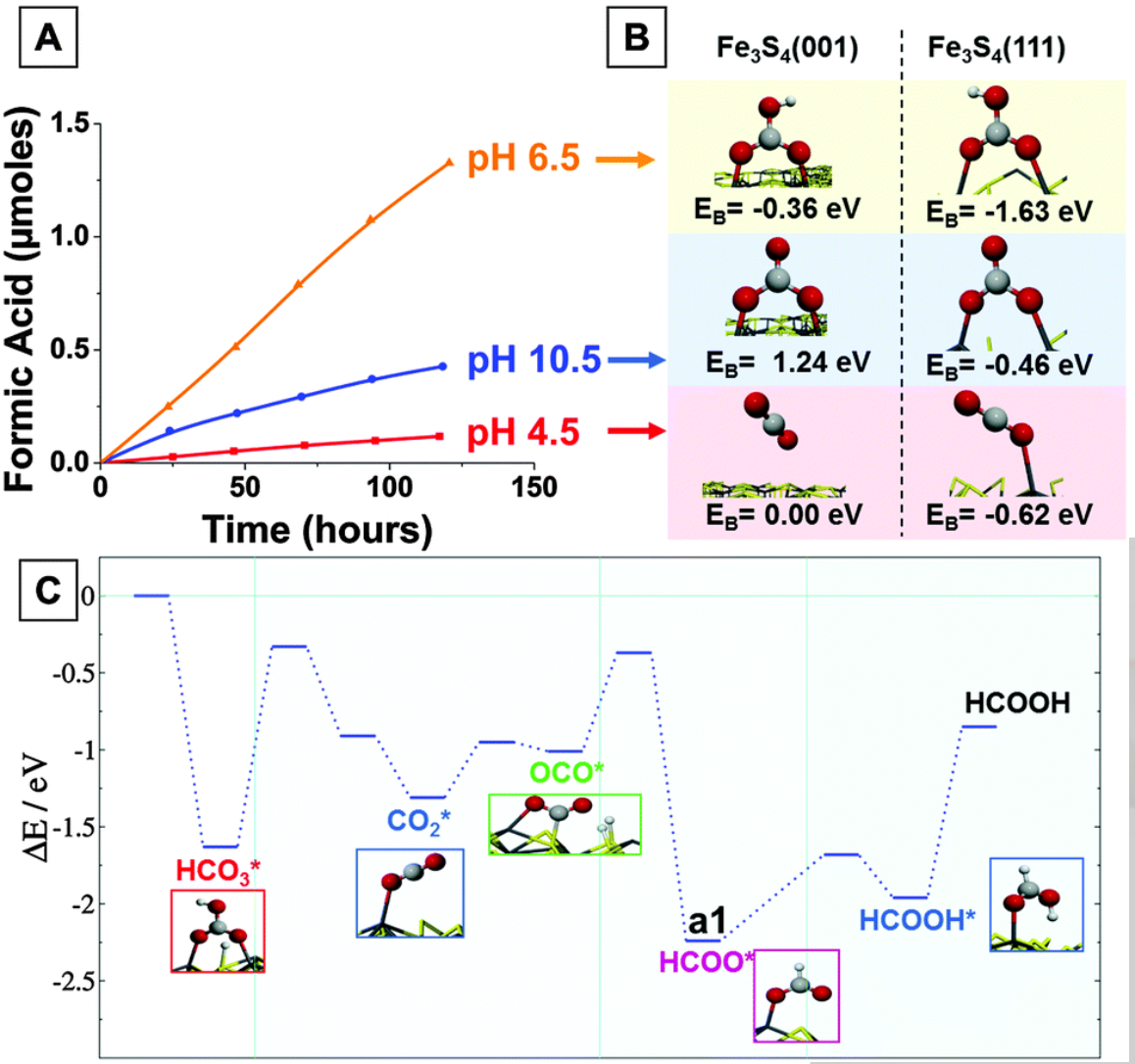


Fig. 2 (A) Formic acid formation as a function of time under different pH conditions; (B) representation of reactants on both the (001) and (111) surfaces as a function of the solution pH, binding energies (E_B) provided as inset; (C) potential energy surface for the mechanism of HCO_3^- reduction to HCOOH on the Fe_3S_4(111). Adsorbed intermediate species are denoted by * and their proposed structures are shown as insets in the figure.

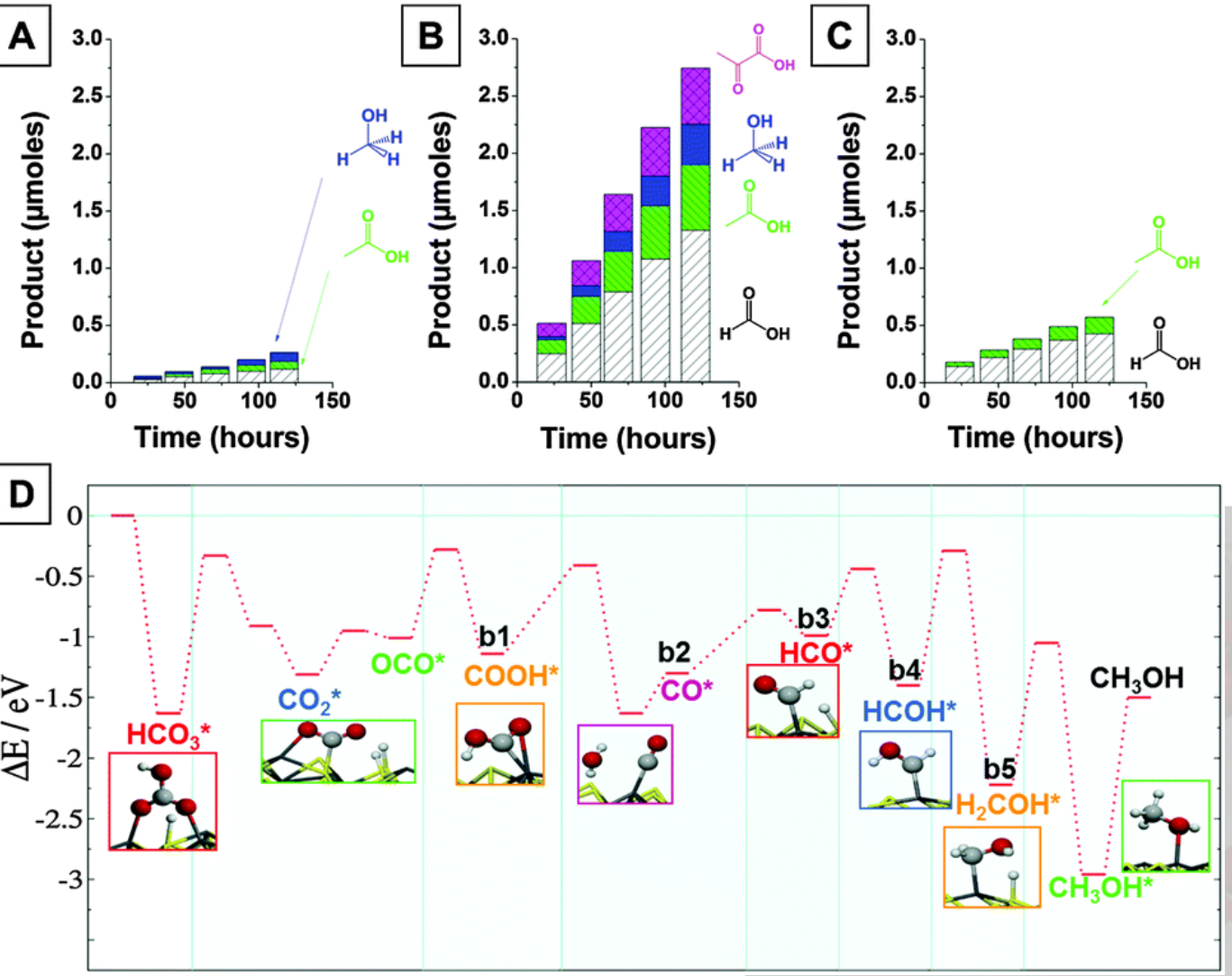
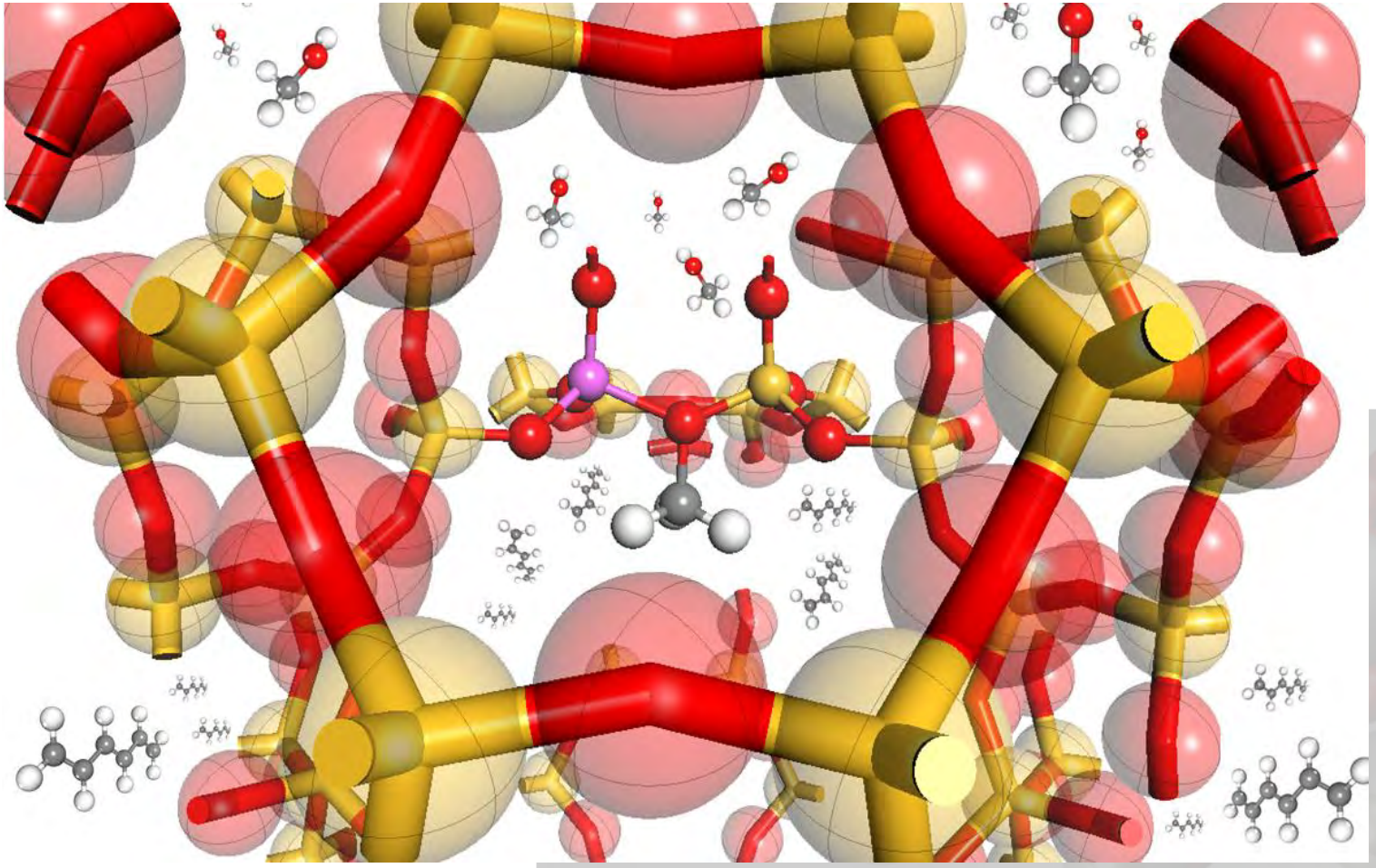


Fig. 3 Formation of formic acid, acetic acid, methanol and pyruvic acid at (A) pH = 4.5; (B) pH = 6.5; (C) pH = 10.5. (D) Potential energy profile for the mechanism of HCO_3^- reduction to CH_3OH, on the $Fe_3S_4(111)$.

Studying the Methanol-to-Hydrocarbons Process

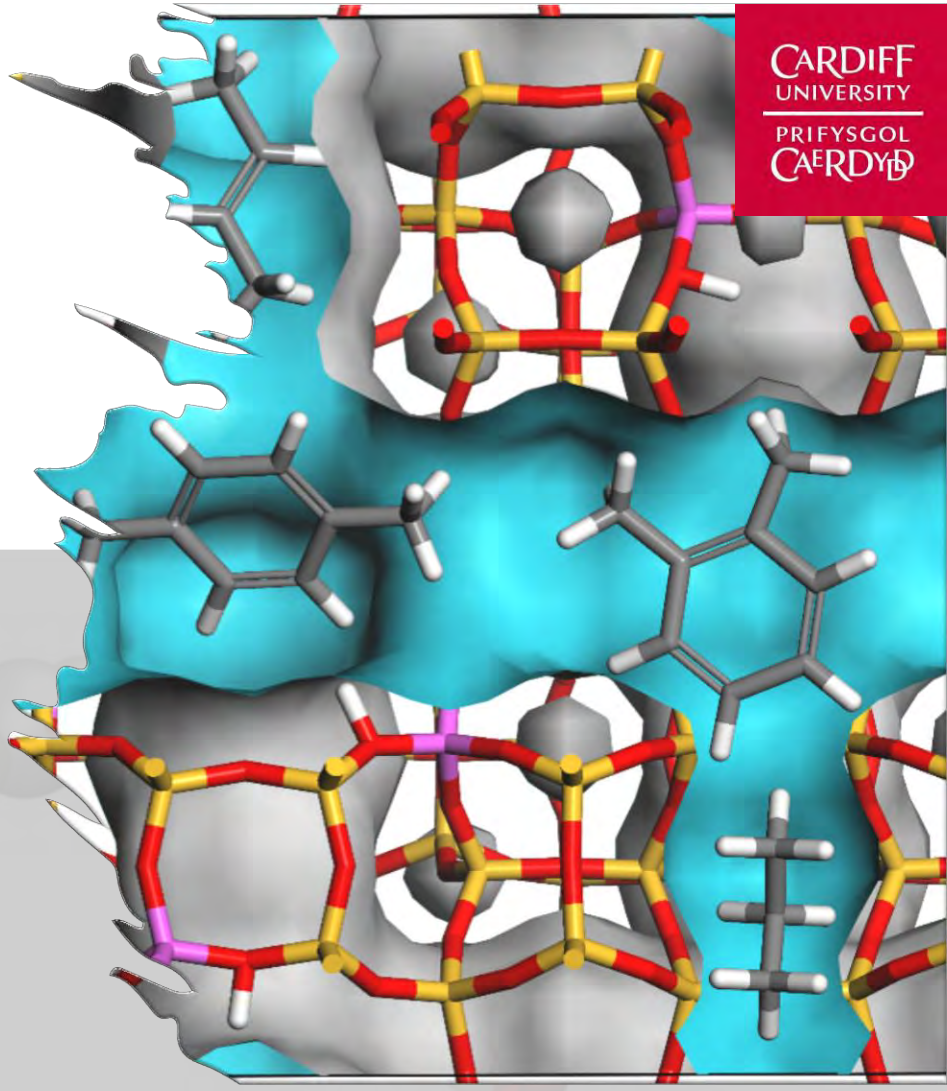


(4 6). A. J. O'Malley; S. F. Parker.; A. Chutia; M. R. Farrow; I. P. Silverwood; V. Garcia-Sakai; C. R. A. Catlow, *Chemical Communications* **2016**, *52*, 2897-2900.

Introduction

- Methanol to hydrocarbons (MTH) → better alternative to conventional octane-grade gasoline & olefins production
- The “hydrocarbon pool” mechanism → not completely understood due to the complexity and techniques with limited sensitivity
- Objective: Better understanding of the “hydrocarbon pool” itself and the elementary reaction steps involved by employing complementary techniques → Elastic/Inelastic –Neutron Scattering and IR

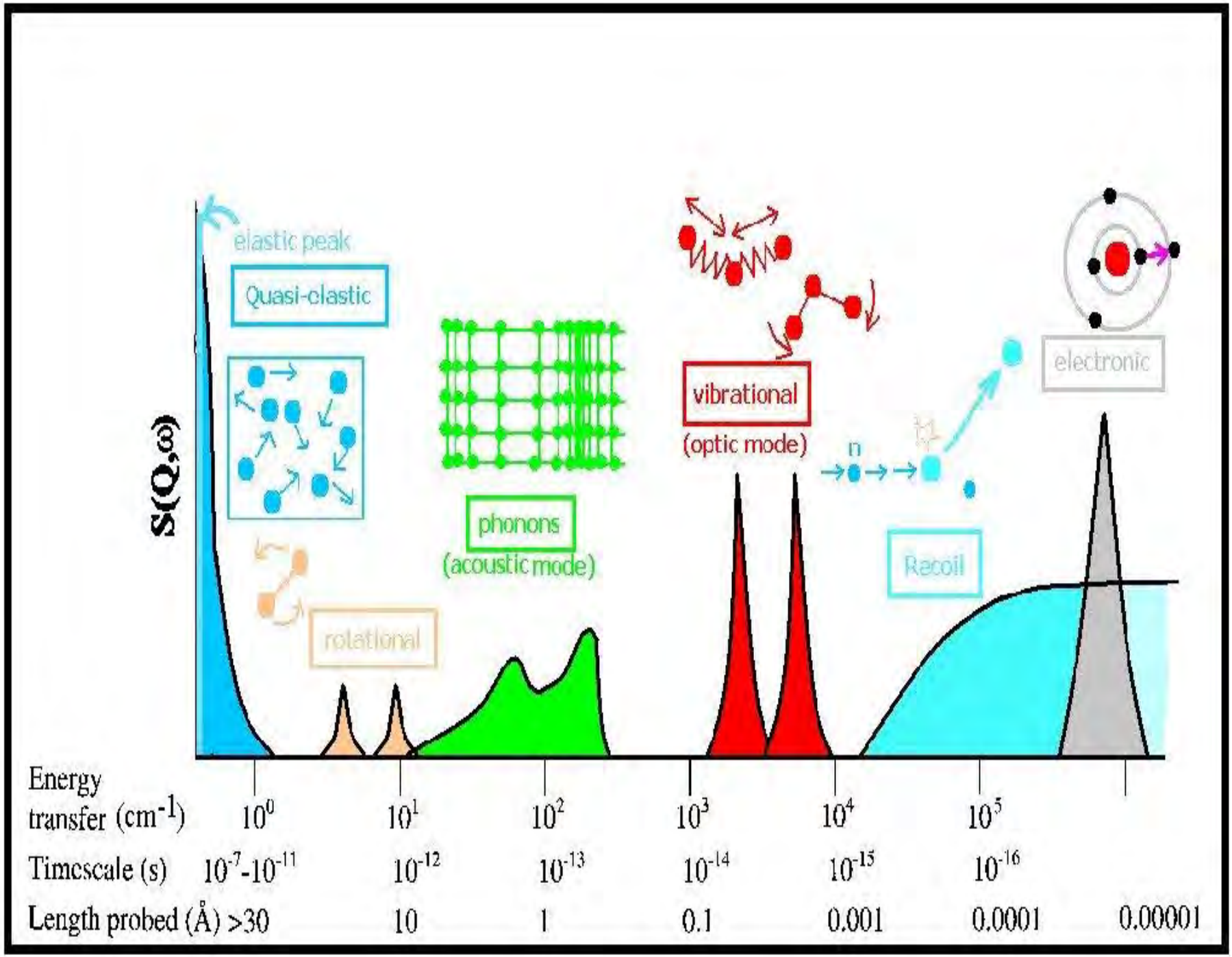
→ The first step: Methanol adsorption, diffusion and reaction



NEUTRON SCATTERING, CATALYSTS and CATALYTIC PROCESSES

- Structure – diffraction (light atoms especially hydrogen)
- Diffusion (QENS)
- Vibrational spectroscopy (INS) – especially for H containing molecules and note the lack of selection rules.

(1) O'Malley, Alexander J., and C. Richard A. Catlow. "Sorbate Dynamics in Zeolite Catalysts" P. 349-401, (2017). Experimental Methods in the Physical Sciences, Vol. 49; Neutron Scattering – Applications in Biology, Chemistry and Materials Science, Edited by F. Fernandez-Alonso and D. L. Price, Academic Press.

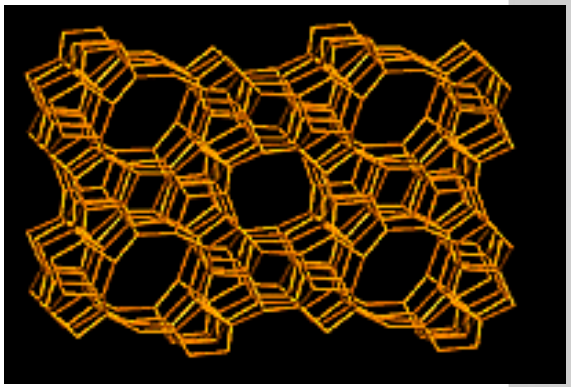

elastic peak
Quasi-clastic
S(Q,ω)
rotational
phonons
(acoustic mode)
vibrational
(optic mode)
n
Recoil
electronic
Energy transfer (cm-1)
10^0
10^1
10^2
10^3
10^4
10^5
Timescale (s)
10-7-10-11
10-12
10-13
10-14
10-15
10-16
Length probed (Å) >30
10
1
0.1
0.001
0.0001
0.00001

Harwell – Rutherford Campus with ISIS and DIAMOND Facilities

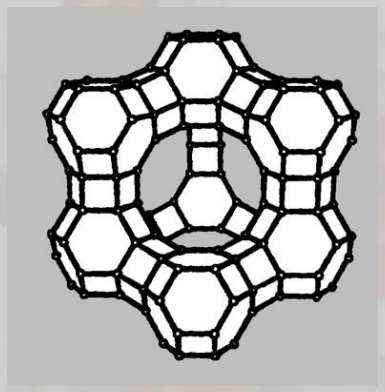
Methoxylation of zeolites – The first step in the Methanol to Gasoline (MTG) Reaction

Alex O'Malley, Ian Silverwood, Stewart Parker, Vicky Garcia-Sakai, A. Chutia and Richard Catlow

(DIFFUSION and REACTION)



H-ZSM-5 – Routine MTG catalyst



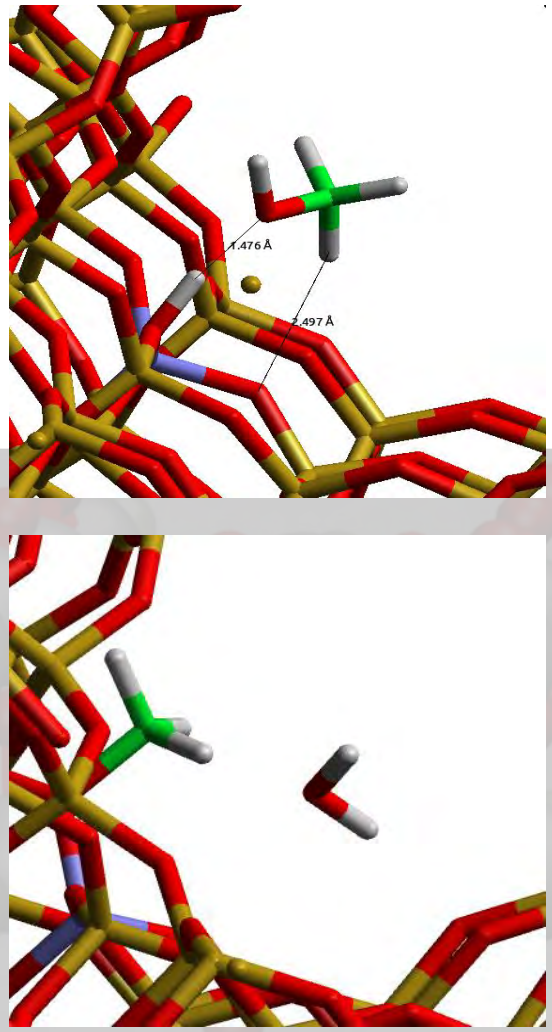
HY – Inactive as an MTG catalyst

Framework dependent room temperature methoxylation in zeolites

- Methanol-to-hydrocarbons (MTH) process is an intensively studied topic in catalytic science

- The initial step is thought to be the condensation reaction of the methanol with the acid framework hydroxyl to create the framework methoxy species.

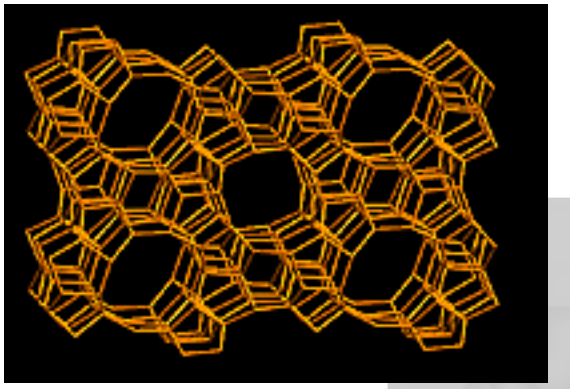
- Previous studies (experimental and computational) predict a significant energy barrier to this process



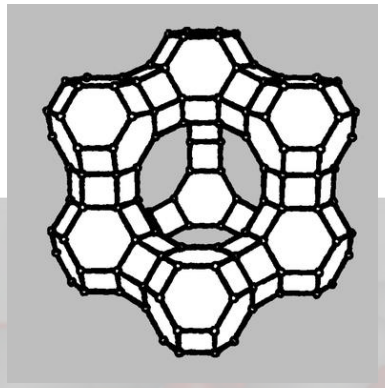
(7). V. van Speybroeck, K. Hemelsoet, L. Joos, M. Waroquier, R. G. Bell, C. Richard. A. Catlow, *Chem. Soc. Rev.* **2015**, *44*, 7044.

Framework dependent room temperature methoxylation in zeolites

- Inelastic neutron scattering (INS) and Quasielastic neutron scattering (QENS) were used to probe the behaviour of methanol in two zeolites:



H-ZSM-5 – Routine MTG catalyst



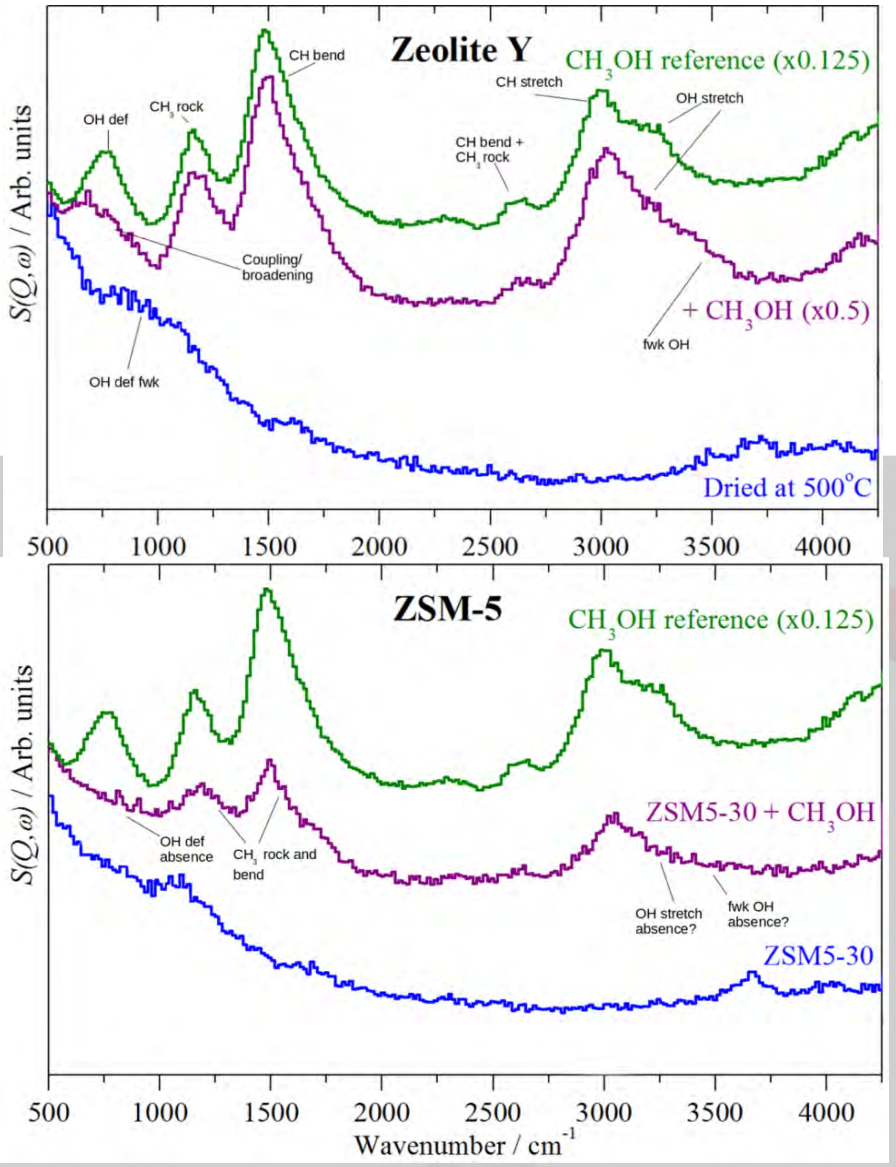
HY – Inactive as an MTG catalyst

- Both samples with the same Si/Al ratio, so the same proportion of acidic sites in each sample.
- Zeolites loaded with methanol at room temperature, QENS carried out using OSIRIS, INS carried out using MAPS.

(6). A. J. O'Malley; S. F. Parker.; C. R. A. Catlow, *Chemical Communications* **2017**, *53*, *1*2164-12176.

Framework dependent room temperature methoxylation in zeolites - INS

- In HY, methanol is shown to H-bond to the framework, through broadening and downshifting of the MeOH deformation and stretching bands.
- Both methanol and framework hydroxyls are intact.
- In H-ZSM-5, methanol OH deformations and stretches disappear.
  - Condensation reaction?
  - No water? (possibly removed in He/Methanol gas stream).
  - Almost instant rather than on a longer time scale in the sealed system.
  - No indication of hydrogen bonded methanol, sensitivity?

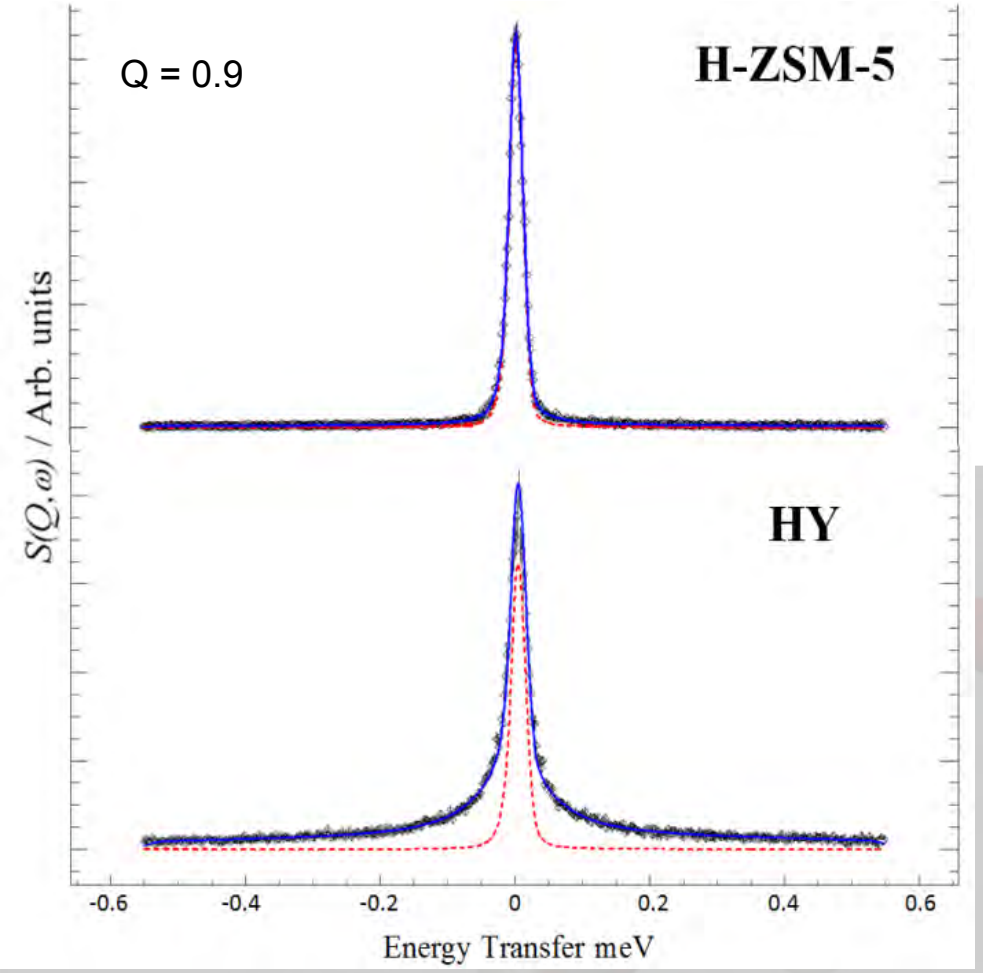


Framework dependent room temperature methoxylation in zeolites - QENS

Support offered by QENS for an immobile methoxy group in ZSM-5

- Significant mobility found in zeolite HY on both rotational and translational scales
  - Lorentzian functions consistent with jump diffusion (between or within cages?) and Fickian diffusion within a confined volume.

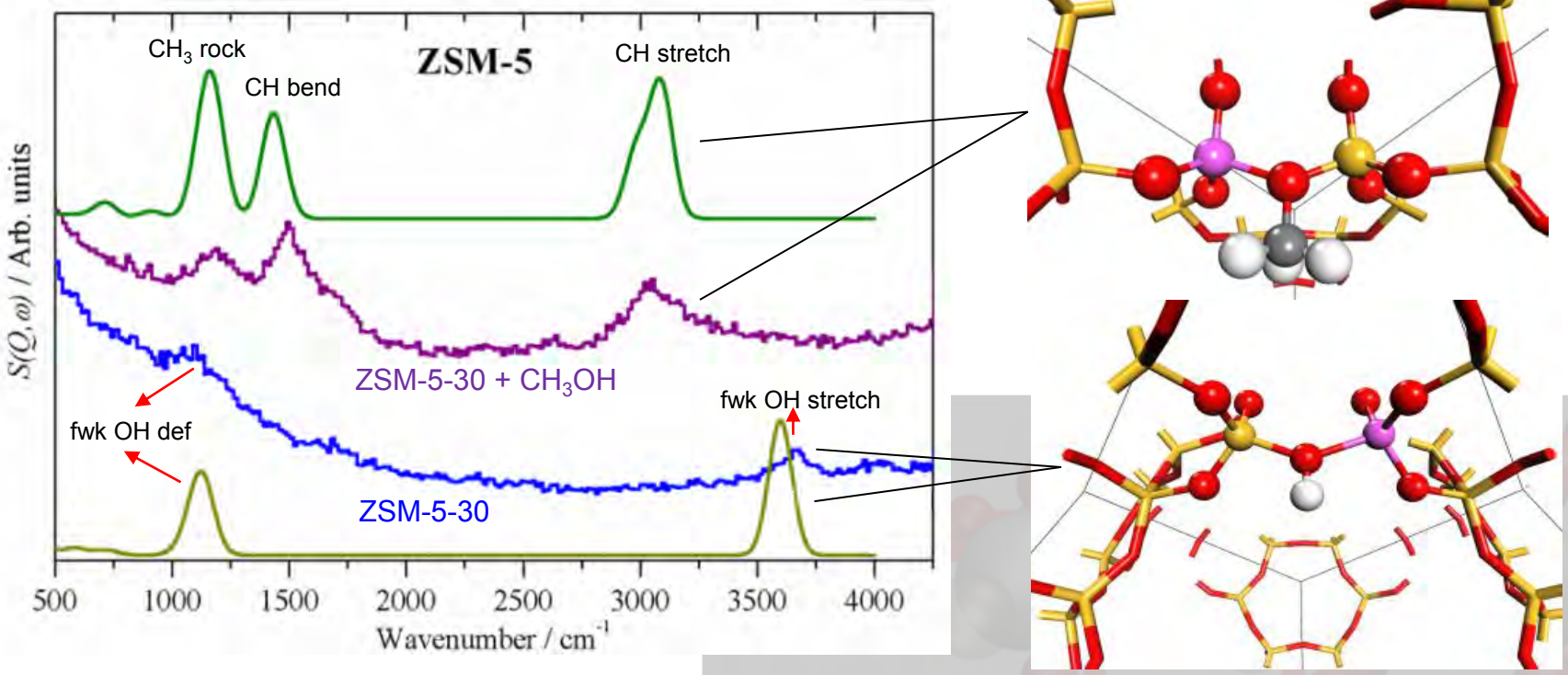
- Methanol shown to be immobile in H-ZSM-5
  - Very close fit to the resolution spectra at 5 K for low Q values
  - Small Lorentzian components at high Q values
  - EISF not able to fit to models derived for rotating methane or methanol
  - No water diffusing (supports methoxylation)



(6). A. J. O'Malley; S. F. Parker.; C. R. A. Catlow et al. *Chemical Communications* **2016**, *52*, 2897-2900.

(8). S. K. Matam; A. J. O'Malley; S. F. Parker.; C. R. A. Catlow et al. *RSC Catal. Sci. Technol.* **2018**, *8*, 3304-3312

Framework dependent room temperature methoxylation in zeolites - simulations



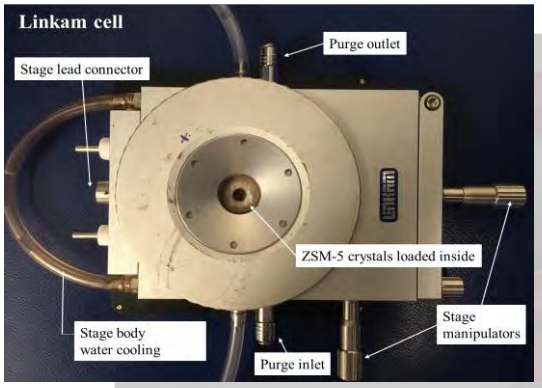
- Theoretical vibrational spectra calculated using CASTEP for phonon calculations and ACLIMAX accounting for scattering cross section.
- Excellent agreement shown for a framework methoxy species.

(6). A. J. O'Malley; S. F. Parker.; C. R. A. Catlow et al. *Chemical Communications* **2016**, *52,* 2897-2900.

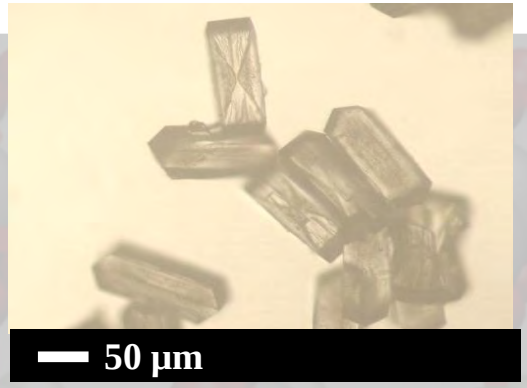
The role of methoxy species in the first C-C bond formation

Synchrotron Operando Infrared Microspectroscopy (OIMS) at B22

IR microscope



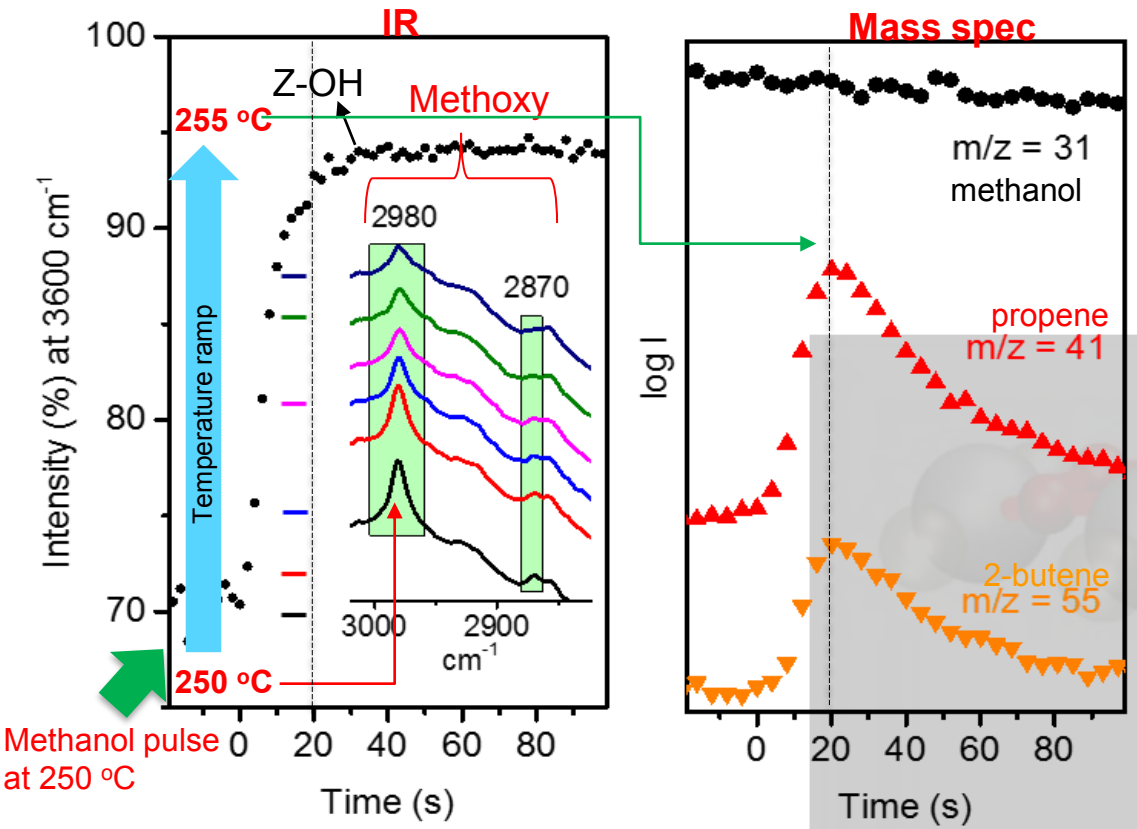
IR reaction cell

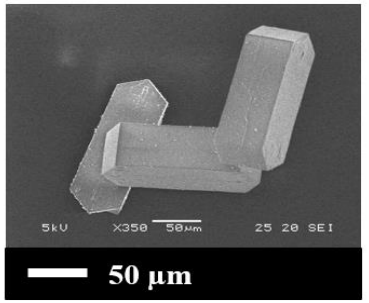


H-ZSM-5 crystals (Si/Al = 30)

The role of methoxy species in the first C – C bond formation

Experimental : H-ZSM-5 single crystals were dried at 350 °C for 1h and cooled to 250 °C. A methanol pulse of 8µl was injected and ramped to 255 °C



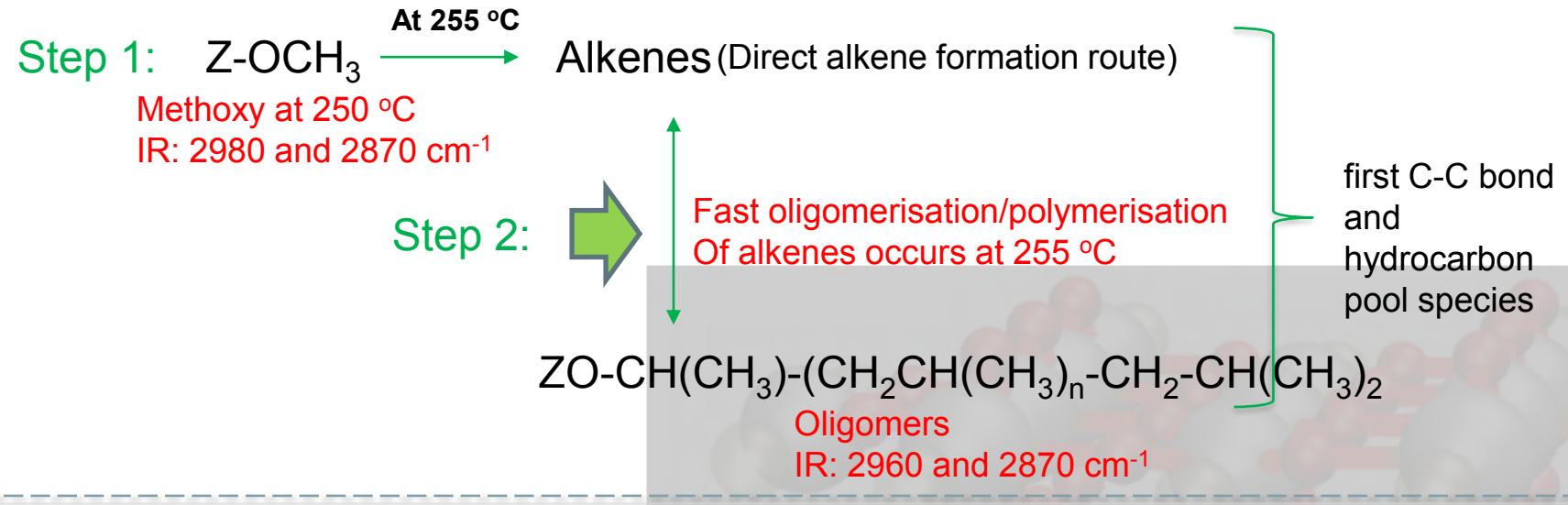


- Methoxy species at 250 °C at the expense of 30% absolute Z-OH
- On heating from 250 to 255 °C → ≈ 80% methoxy are lost and relatively 83% Z-OH are recovered

…..and burst of alkenes appear in MS → note coincidence of diminished methoxy species and regeneration of hydroxyls and alkenes formation as a function time (s) on x-axis

I. Minova, S.K. Matam, C. Richard A. Catlow, R.F. Howe et al., ACS Catal. 9, 6564, 2019

Summary: mechanistic scheme for the initial stage of MTH



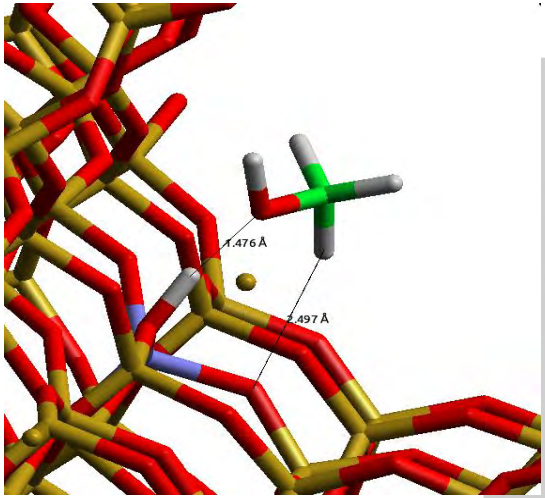
Continues…

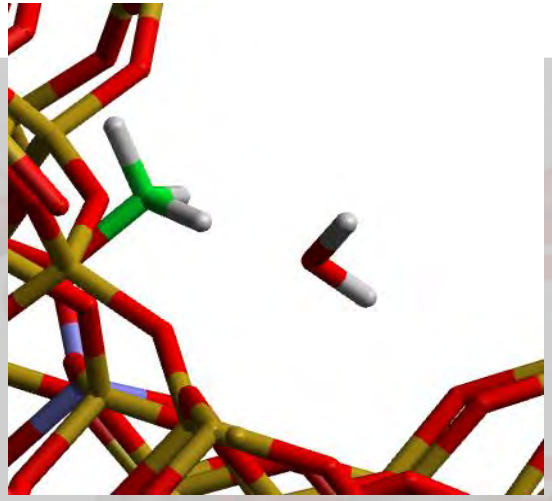
Step 3:

[1] I. Minova, S.K. Matam, C. Richard A. Catlow, R.F. Howe et al., ACS Catal. 9, 6564, **2019;** [2] I. Minova, S.K. Matam, C. Richard A. Catlow, R.F. Howe et al., Phys. Chem. Chem. Phys. **2020**

MTG: do carbenes play a role?

After framework oxygen methoxylation, can the methyl group be deprotonated?





Recent synchrotron IR work suggest possible role of carbenes on first C-C bond formation

Elementary Steps in the Formation of Hydrocarbons from Surface Methoxy Groups in HZSM-5 Seen by Synchrotron Infrared Microspectroscopy

Ivalina B. Minova, Santhosh K. Matam, Alex Greenaway, C. Richard A. Catlow, Mark D. Frogley, Gianfelice Cinque, Paul A. Wright, Russell F. Howe* , ACS Catalysis 9, 6564-6570 (2019)

BUT

Calculations suggest high activation energies for deprotonation of methoxy groups

Generation of Carbenes during Methanol Conversion over Brönsted Acidic Aluminosilicates. A Computational Study

•P. E. Sinclair and C. R. A. Catlow *J. Phys. Chem. B* 1997, 101, 3, 295–298

Eact ~ 215-232 KJ/mole

Concerted not stepwise mechanism?

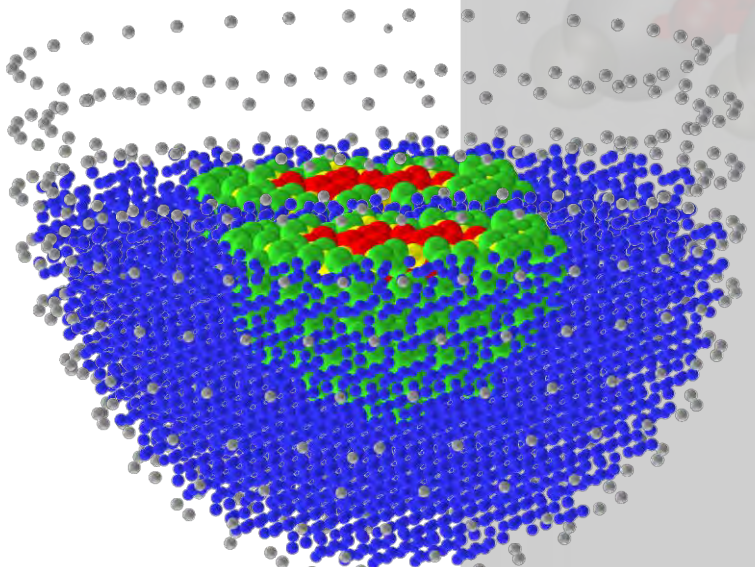
CARDIFF UNIVERSITY
PRIFYSGOL CAERDYDD

UCL

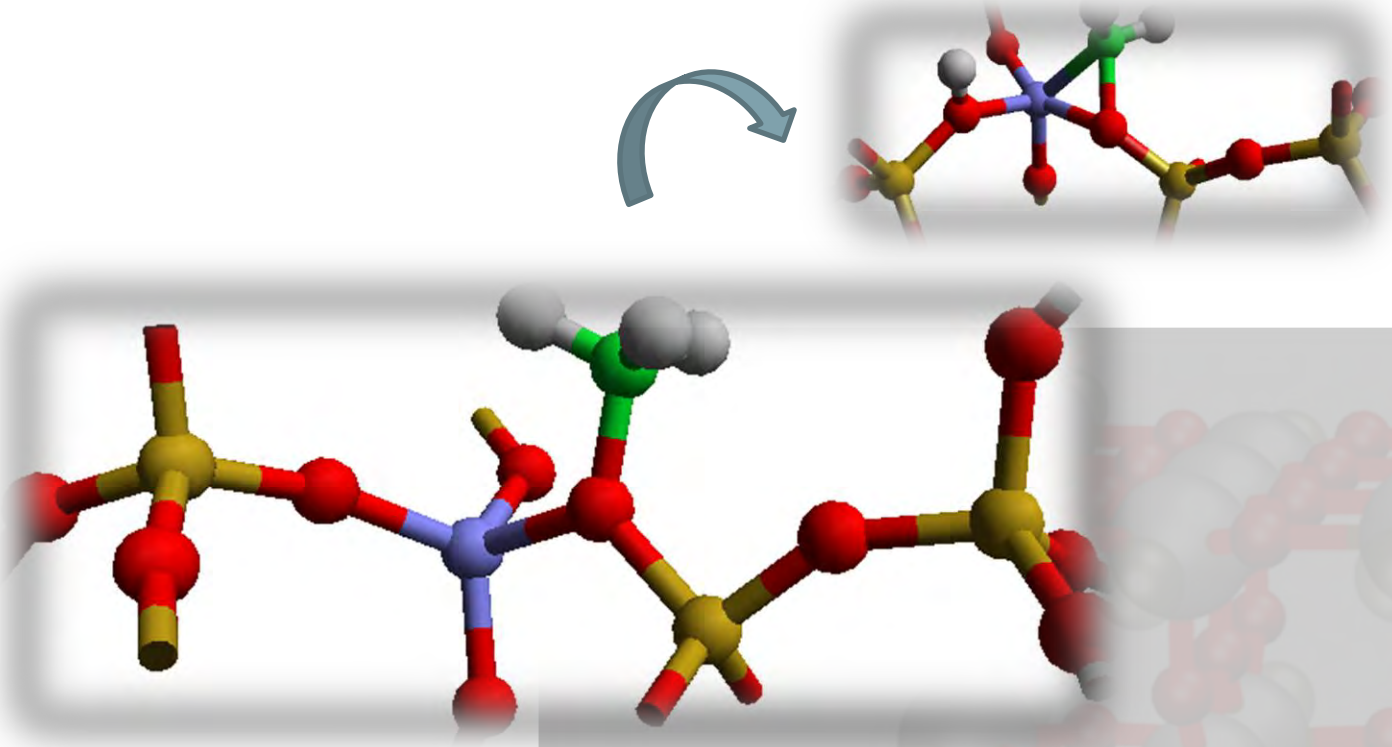
QM/MM Techniques:

Most DFT calculations in catalytic science use periodic methods, (especially using the VASP code), but QM/MM:

- Avoid limitations of periodic methods
- Allows highly accurate methods to be used in QM Core
- Successfully applied to enzymes, zeolites and oxides, but challenges in extending to other systems

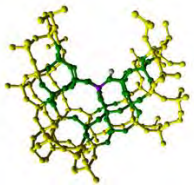


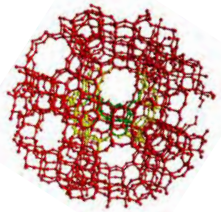
QM/MM study of the stability of methoxy and carbene in zeolite H-ZSM-5



QM/MM study of the stability of carbene in zeolite H-ZSM-5

QM/MM: Embedded cluster modelling



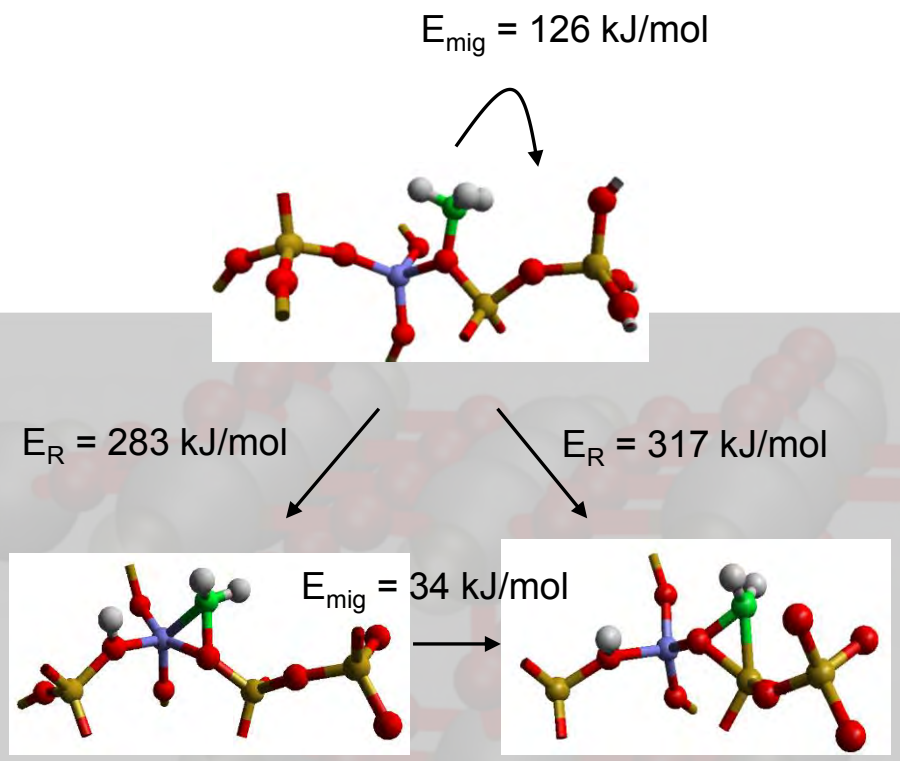


Methodology

- Chemshell software for hybrid QM/MM static calculations;
- QM calculations: DFT, B97-3, NWChem
- MM calculations: forcefield, DL-Poly

Observations

- Methoxy conversion is very endothermic
- Carbene stabilises within the zeolite framework with a high exothermic bonding energy (~ -150 kJ/mol)
- Carbene or methoxy migration away from the active site is thermodynamically unfeasible



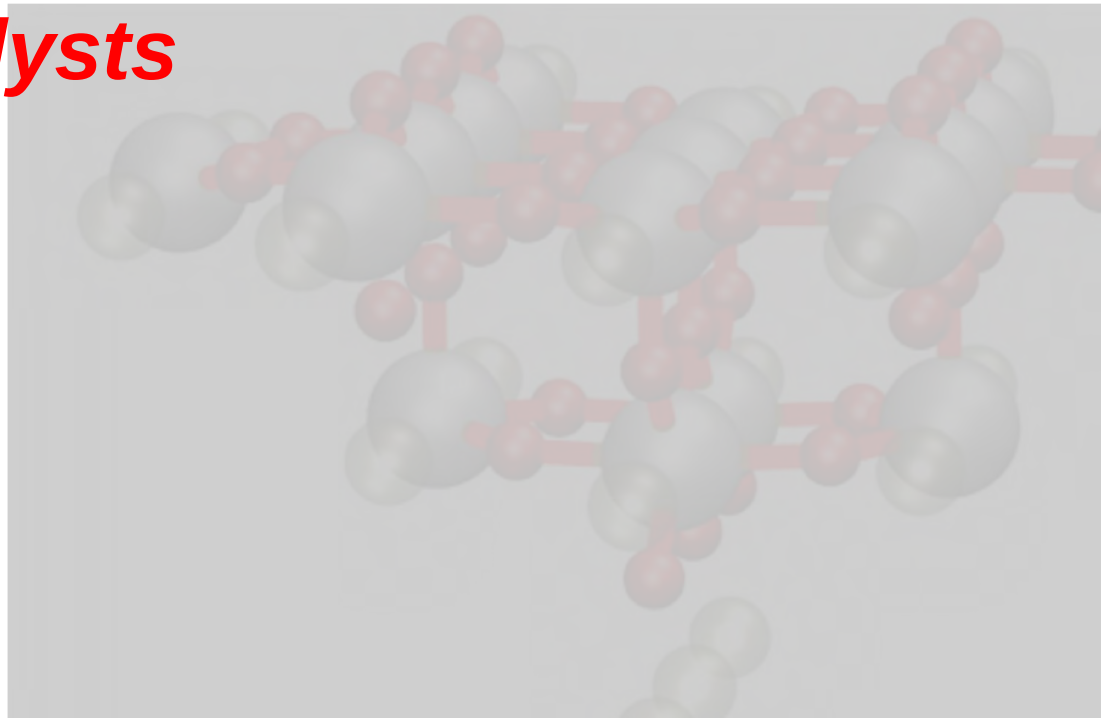
S. A. F. Nastase, A. J. Logsdail, C.R.A Catlow, PCCP – in press,

CARDIFF UNIVERSITY
PRIFYSGOL CAERDYDD

UCL

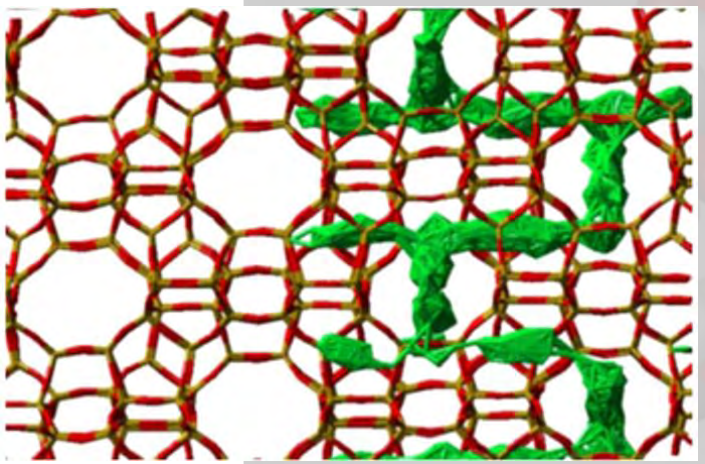
THEME TWO

Application of computational and neutron scattering techniques to the *dynamics and reactivity of sorbed molecules in microporous catalysts*



Quasi- Elastic and Molecular Dynamics Scattering Studies of Hydrocarbon Dynamics in Zeolites

Alex O'Malley, Stewart Parker, Vicky Garcia-Sakai, Sanghamitra Mukhopadhyay and Richard Catlow



(1) O'Malley, Alexander J., and C. Richard A. Catlow. "Sorbate Dynamics in Zeolite Catalysts" P. 349-401, (2017). Experimental Methods in the Physical Sciences, Vol. 49; Neutron Scattering – Applications in Biology, Chemistry and Materials Science, Edited by F. Fernandez-Alonso and D. L. Price, Academic Press.

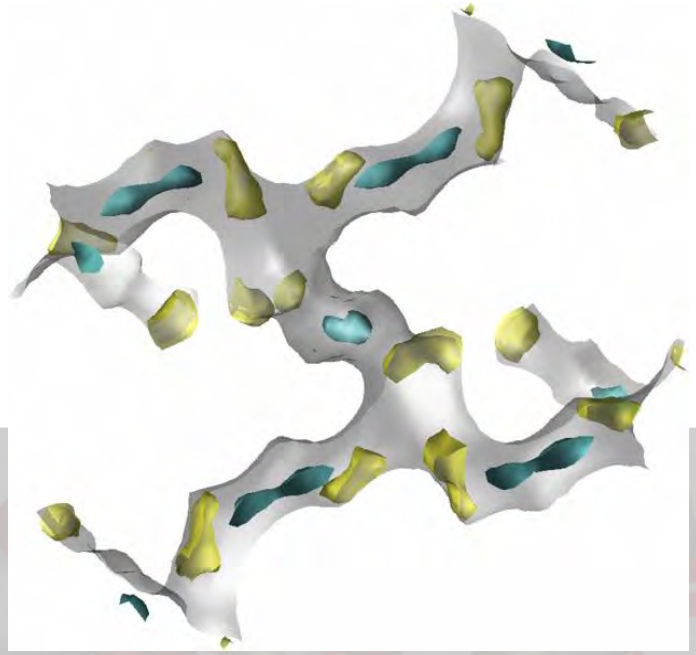
Diffusion of Hydrocarbons in Zeolites

Zeolites most notable for use in the petrochemical industry as molecular sieves and as shape selective acidic catalysts

Understanding of diffusion processes essential

- Separation processes rely on significant differences in diffusion coefficients of the components.

- The rate limiting step of a catalytic process may be in diffusion of components to and from the active site.



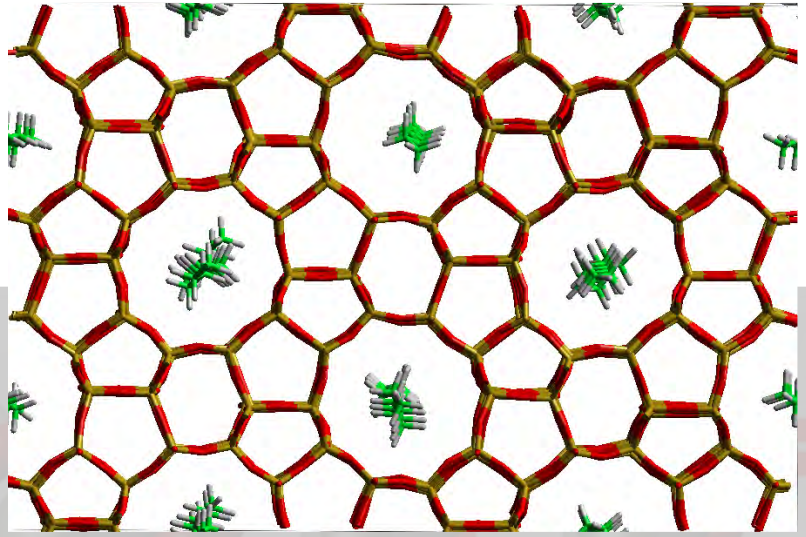
Centre of mass distributions for butane (blue) and Methane (green) in silicalite (1)

Difficult, as all this happens inside the zeolite. Computational methods such as molecular dynamics simulations are desirable

(~~1~~2) Gergidis, Leonidas N., Doros N. Theodorou, and Hervé Jobic. "Dynamics of n-butane-methane mixtures in silicalite, using quasielastic neutron scattering and molecular dynamics simulations." The Journal of Physical Chemistry B 104.23 (2000): 5541-5552.

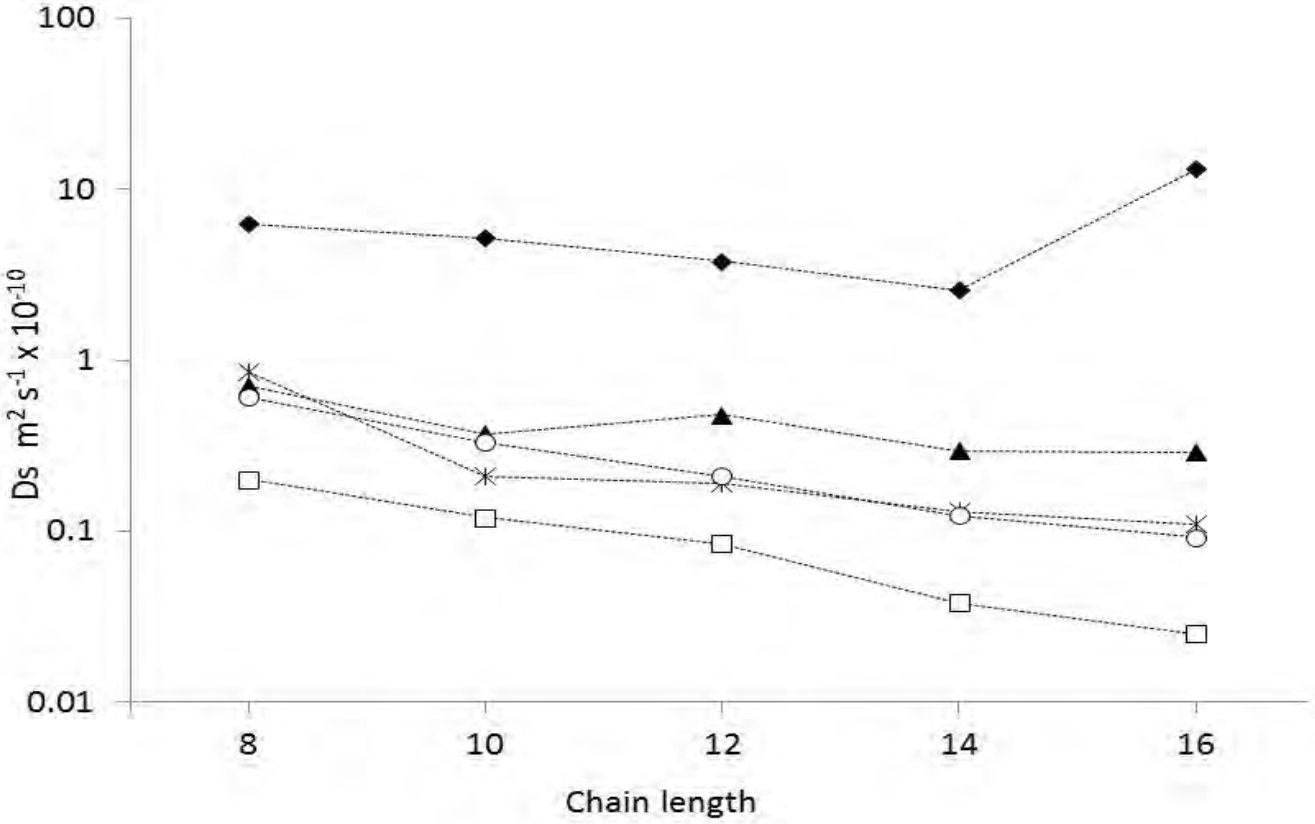
Longer *n*-alkanes in silicalite: Detailed MD models giving closer agreement with QENS

- C_8 – C_{20} in silicalite - directly compared with QENS studies by Jobic (2).
- Used the same loadings as experiment e.g. 1.56 mol/uc
- Use flexible frameworks and all-atom hydrocarbon potentials
- Same temperature range to calculate diffusion coefficients and activation energy.



(23) Hervé Jobic*,† and and Doros N. Theodorou‡ The Journal of Physical Chemistry B 2006 110 (5), 1964-1967

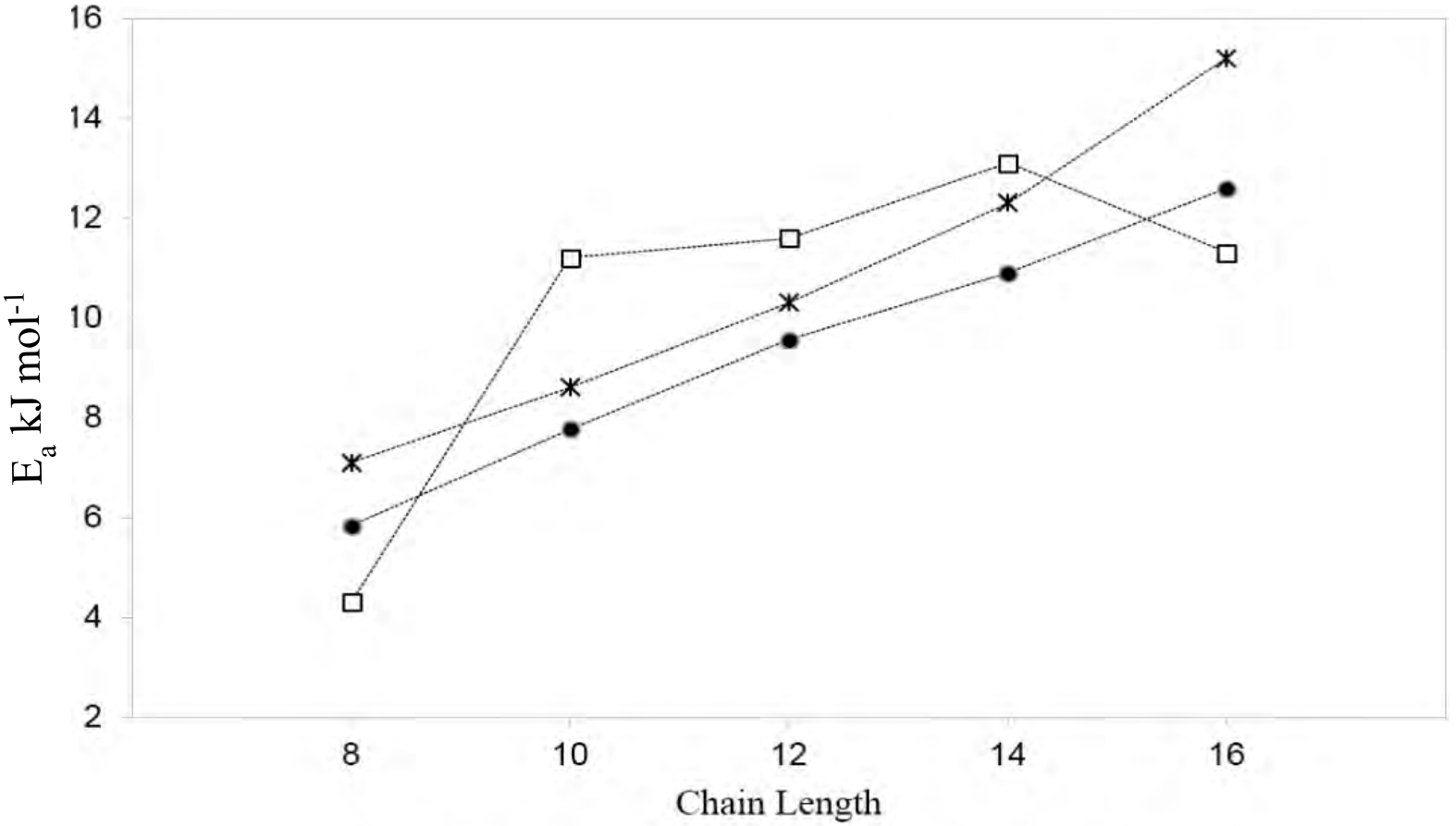
Diffusion coefficients: Compare simple MD models, hierarchical simulations, current study



A plot of the calculated diffusion coefficients from the current MD simulations (O), MD simulations at infinite dilution (▲)[1], MD simulations using simpler models (▲), Hierarchical simulations (∗) and QENS studies (□) .

(3~~-~~4). O'Malley, Alexander J., and C. Richard A. Catlow. "Molecular dynamics simulations of longer n-alkanes in silicalite: a comparison of framework and hydrocarbon models." *Phys. Chem. Chem. Phys.* 15.43 (2013): 19024-19030.

Activation energies: QENS, Hierarchical simulations, current MD simulations



A plot of the activation energy of diffusion with chain length, for the current MD study (•) , QENS studies (∗) and hierarchical simulations (□)

(4 5). O'Malley, Alexander J., and C. Richard A. Catlow. "Molecular dynamics simulations of longer n-alkanes in silicalite: Up-to-date models giving close agreement with experiment." *Phys. Chem. Chem. Phys.* – 2015

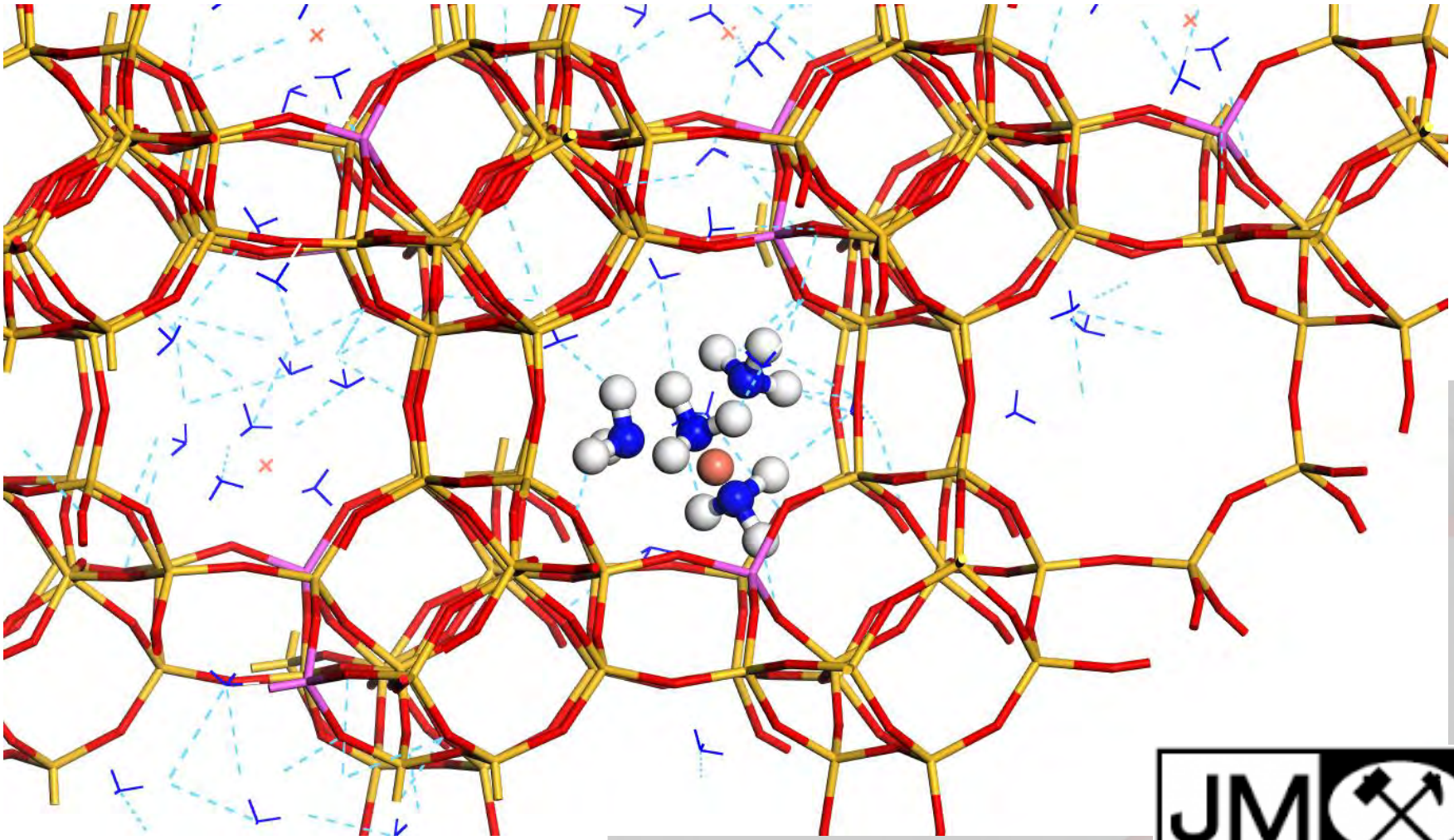
QENS - Studies of Hydrocarbon Dynamics in Zeolites: Summary

- Closer agreement between MD and QENS diffusion coefficients for hydrocarbons in zeolites – complementarity allows detailed understanding of dynamical processes

- Diffusion behaviour can be signature for reaction

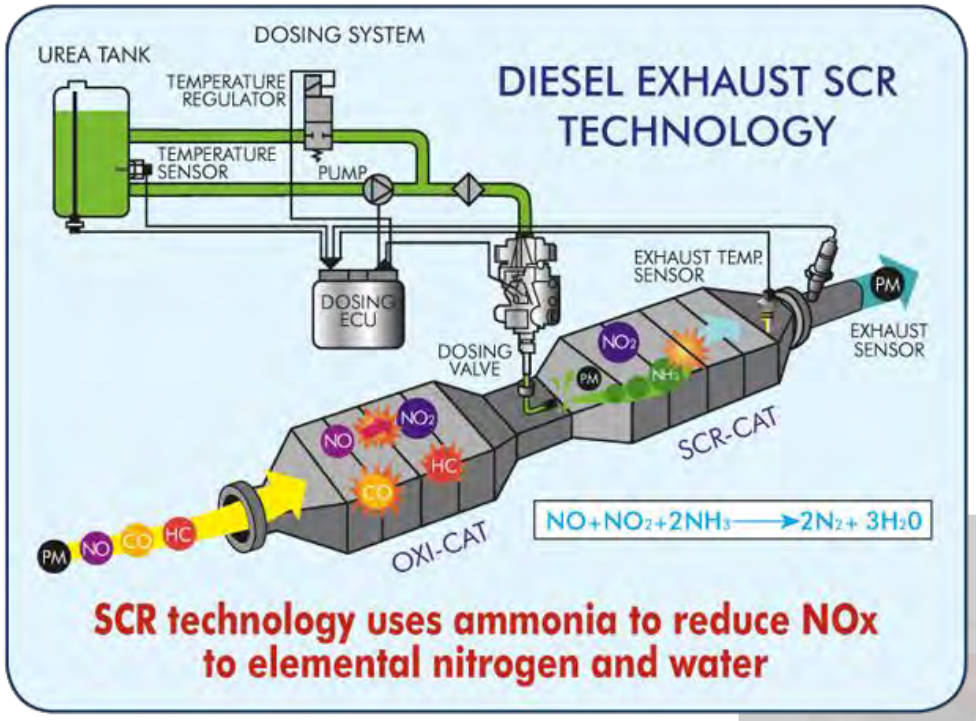
(1) O'Malley, Alexander J., and C. Richard A. Catlow. "Sorbate Dynamics in Zeolite Catalysts" P. 349-401, (2017). Experimental Methods in the Physical Sciences, Vol. 49; Neutron Scattering – Applications in Biology, Chemistry and Materials Science, Edited by F. Fernandez-Alonso and D. L. Price, Academic Press.

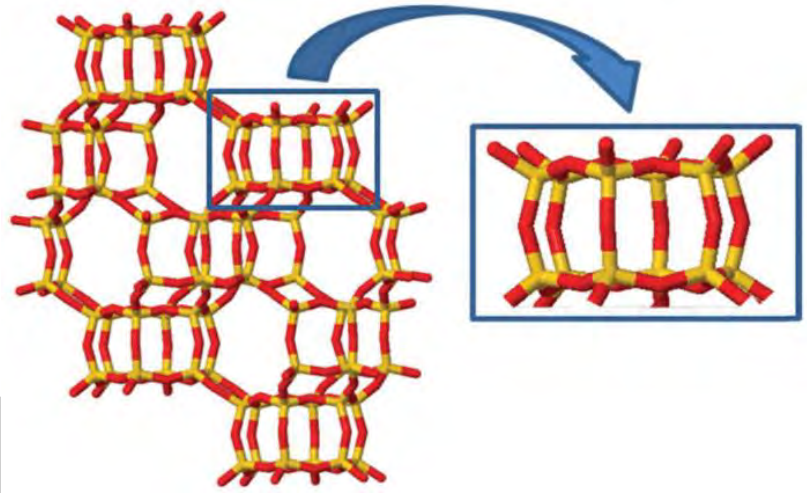
Ammonia Mobility in Chabazite: Insight into the Diffusion Component of the NH_3-SCR Process



(9). A. J. O'Malley., M. Sarwar, J. Armstrong, C. R. A. Catlow et al., *Phys. Chem. Chem. Phys.* 20, **2018:** 11976-11986.

Cu-Chabazite: The SCR Process

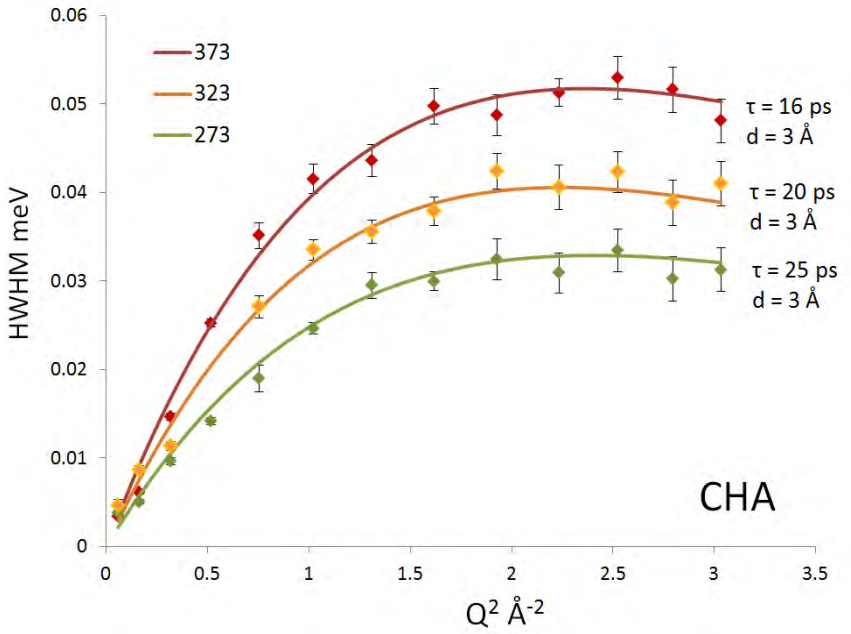


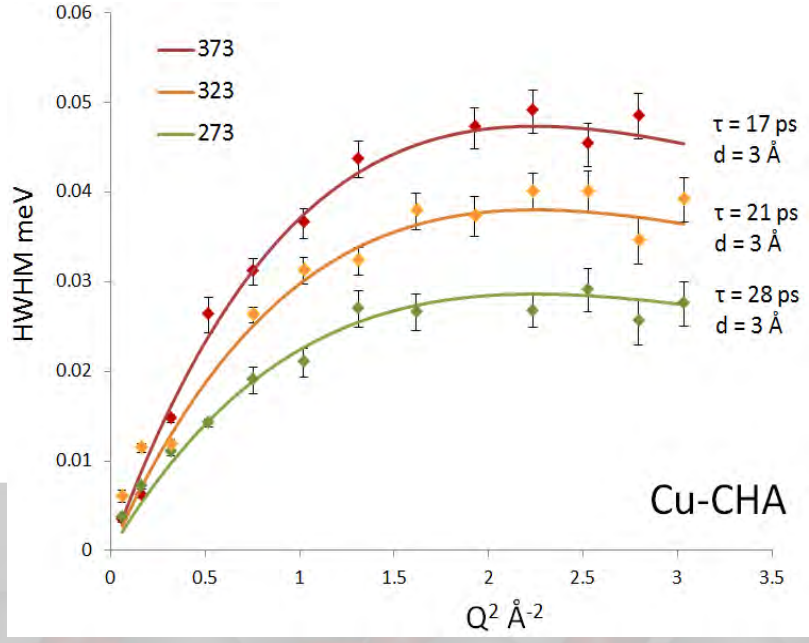


- Collaboration with Johnson Matthey using QENS to study the diffusion of ammonia in CHA and Cu-CHA, to determine th effect of counter ion presence on diffusion.
- Small pore zeolite (3.8 x 3.8 Å) – counterion location variable…

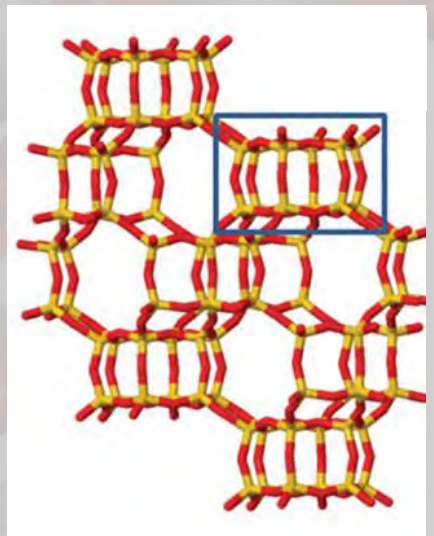
(9). A. J. O'Malley., M. Sarwar, J. Armstrong, C. R. A. Catlow et al., *Phys. Chem. Chem. Phys.* 20, **2018:** 11976-11986.

Ammonia Diffusion in Chabazite as a Function of Cu Counterion Presence – The SCR Process



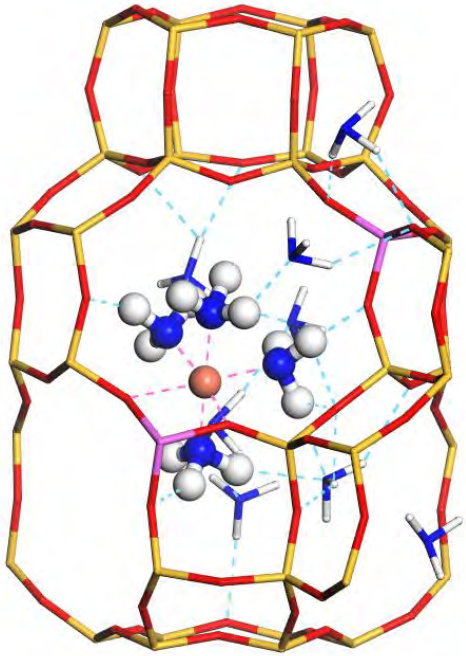


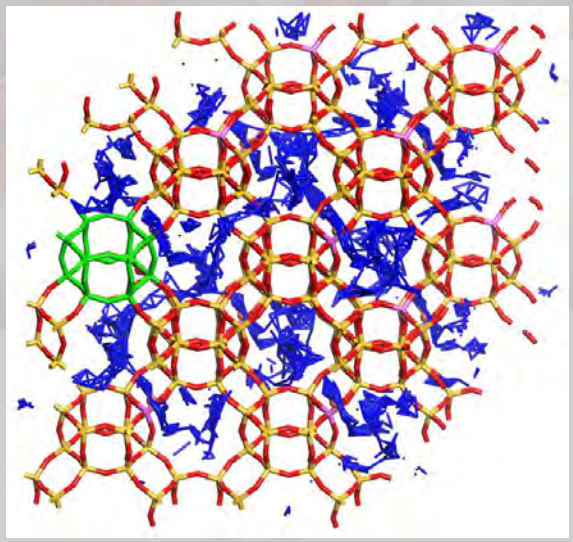
- Ammonia seems to behave basically the same in both zeolites..
- Jump distance of 3 Å, similar residence times at each temperature (16-28 ps)
- More likely through 8-ring than 6-ring?
- Why is the copper ion not changing anything..?



Ammonia Diffusion in Chabazite as a Function of Cu Counterion Presence – The SCR Process

- MD shows clusters of NH_3 coordinated to the Cu^{2+}.
- 'Shell' effectively shields the remaining NH_3 from the potential sink of the Cu^{2+}.
- The coordinated NH_3 moved far too slowly to be detected by the OSIRIS instrument – so is not measured (NSE?)
- Trajectory plots appear to confirm that diffusion is dominant through 8-rings
- Cu^{2+} shell allows intercage diffusion through 8-ring to carry on unimpeded.
- Future experiment introducing deuterated *n*-alkanes into the system.





THEME THREE
The mechanism of ammonia synthesis on transition metal nitrides

Combination of theoretical and in situ experimental investigations of the role of lithium dopant in manganese nitride: a two-stage reagent for ammonia synthesis

Said Laassiri, Constantinos D. Zeinalipour-Yazdi, Nicolas Bion, Richard A. Catlow and Justin S. J. Hargreaves

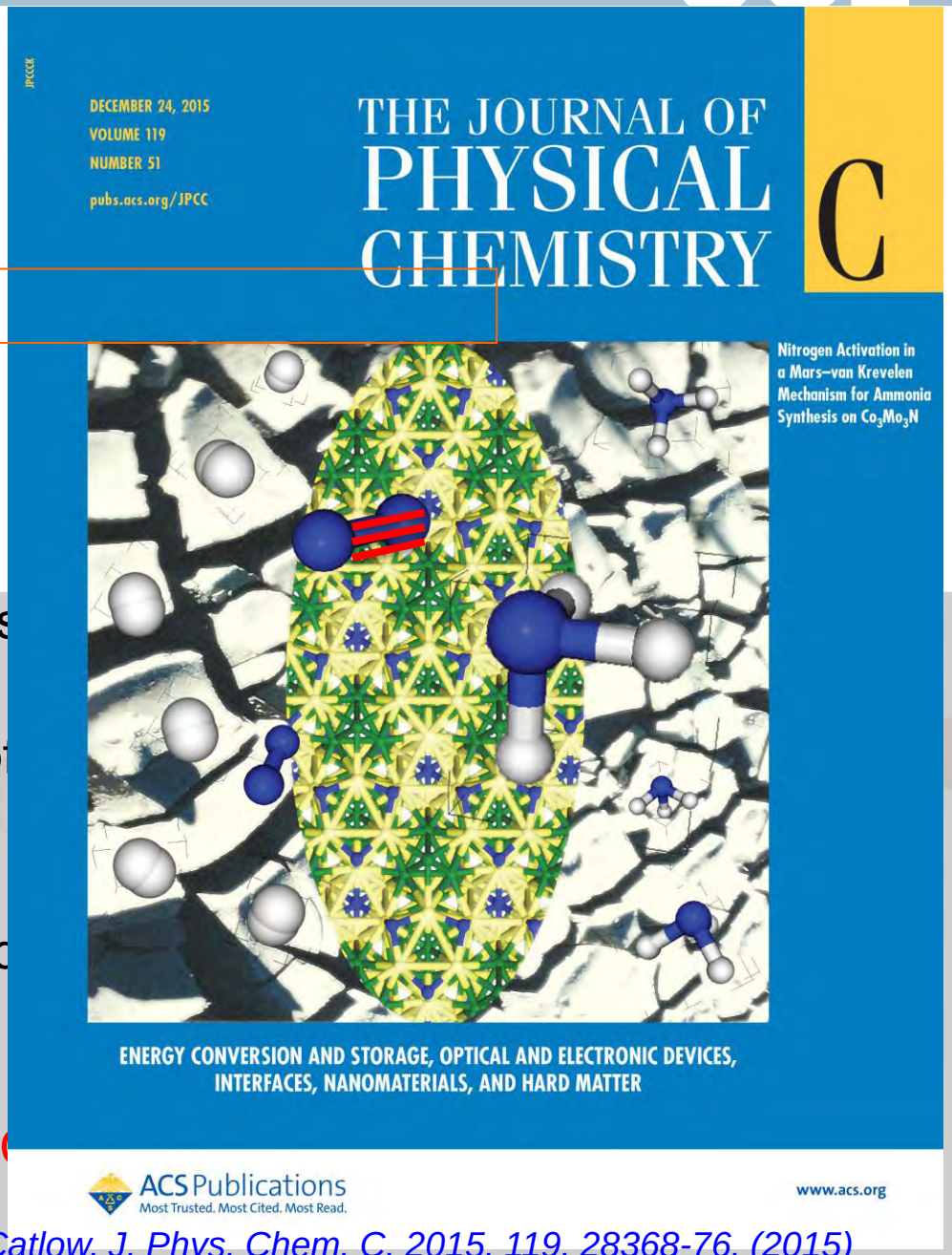
earlier computational work of C.D. Zeinalipour-Yazdi, et al. J. Phys. Chem. C, 2015, 119, 28368-76. (2015)

INTRODUCTION

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ ΔH° = - 45.8 kJ/mol

ΔH_{diss} = 942 kJ/mol

- The reaction is exothermic therefore low T will shift the reaction towards the products → however low temperatures the reaction rate is small therefore it is better to use moderate T
- 4 mole of N_2/H_2 produce 2 mole of ammonia → High P will shift the reaction towards the products
- The Fe potassium oxide promoted catalyst uses T = 400-500 ° C, P 100-200 atm
- Find catalyst that works at 300 ° C → to save energy

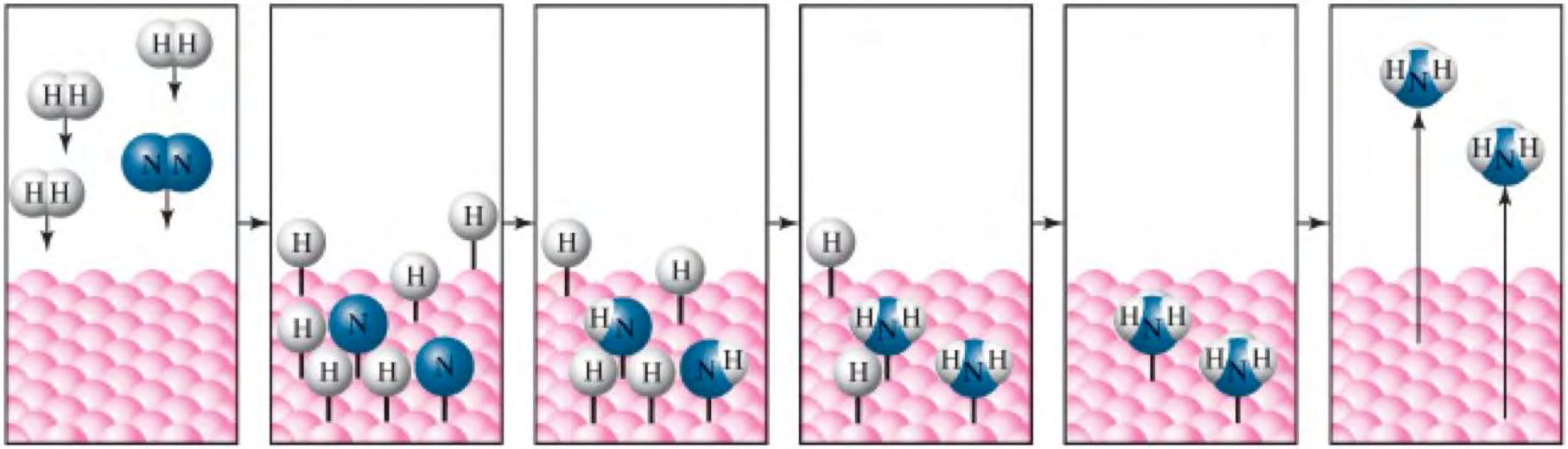


C.D. Zeinalipour-Yazdi, J.S.J. Hargreaves., C.R.A. Catlow, J. Phys. Chem. C, 2015, 119, 28368-76. (2015)

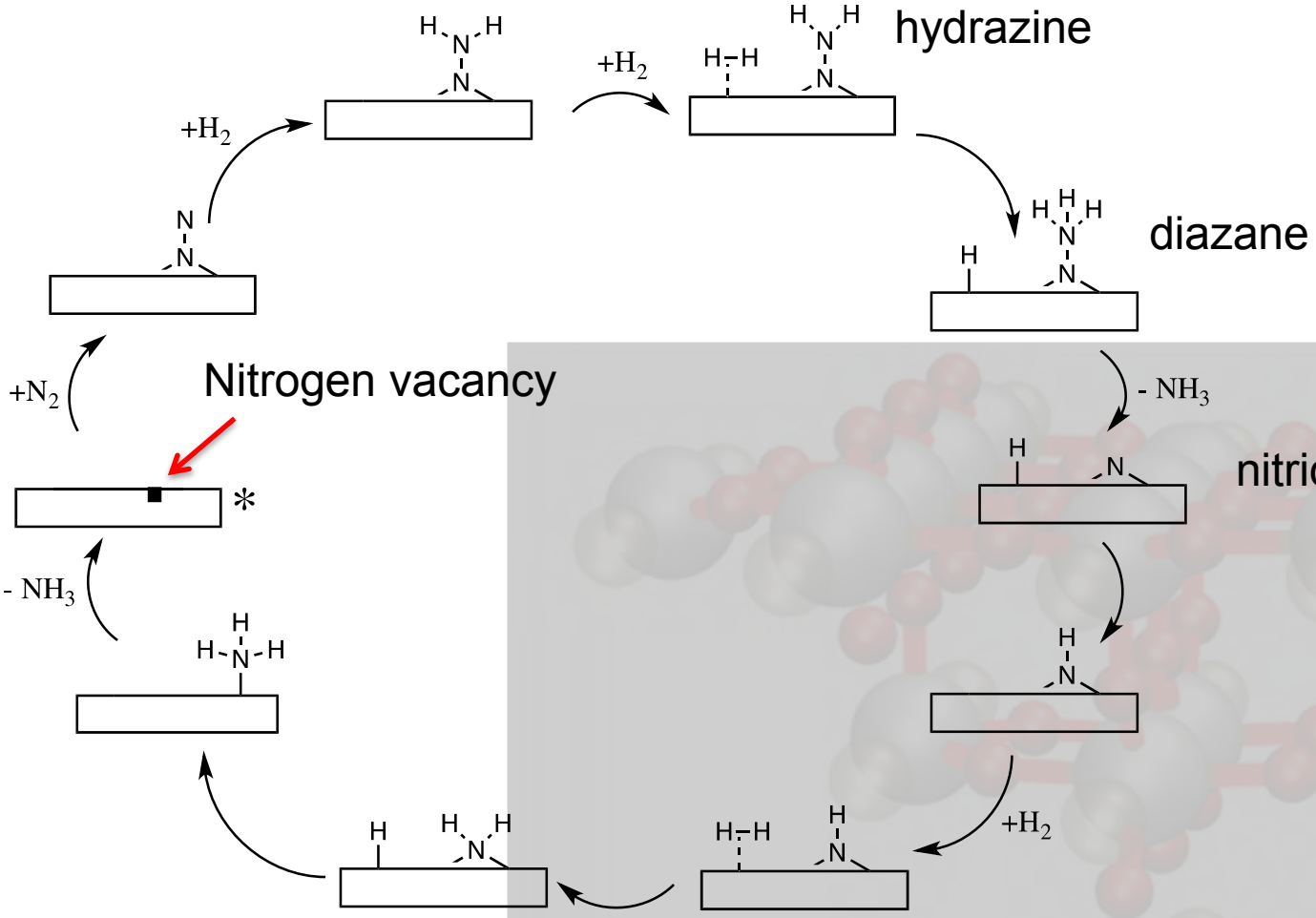
Haber-Bosch process

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ = -45.8 \text{ kJ/mol}$$

- The Haber-Bosch Process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia
- The Haber-Bosch synthesis in 1910 → milestone in catalysis
- The reaction is reversible and the production of ammonia is exothermic.
- Alternative transition metal nitride catalysts (Co_3Mo_3N) investigated using theory and experiment

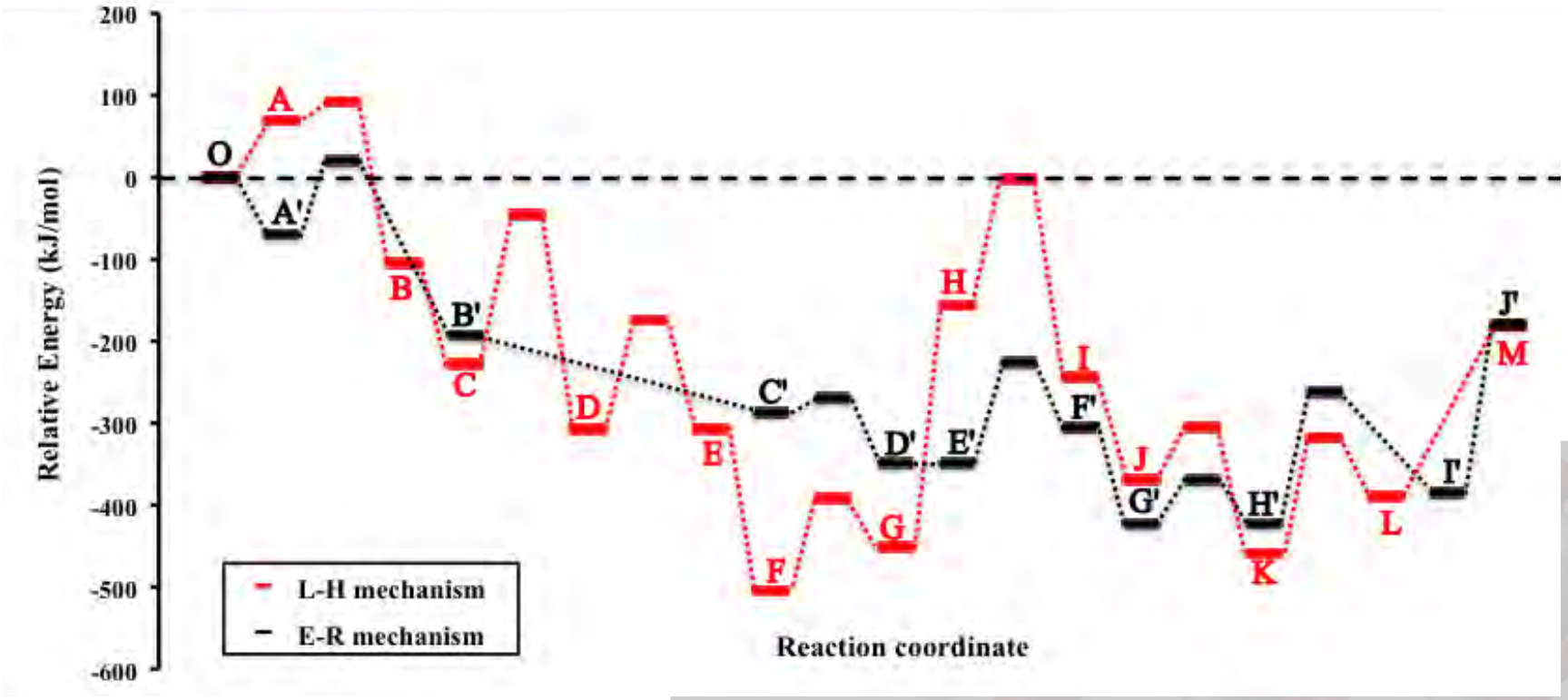


Our proposed non-dissociative mechanism for ammonia synthesis over Co_3Mo_3N



* N_2 chemisorbs to nitrogen vacancies in end-on configuration

PES of two mechanisms



Our mechanism for ammonia synthesis shows that it can occur at milder conditions → Maybe the low temperature ammonia synthesis is possible with Co_3Mo_3N that has a large number of nitrogen vacancies

Zeinalipour-Yazdi, C. D.; Hargreaves, J. S. J.; Catlow, C. R. A., Low-T Mechanism of Ammonia Synthesis on Co_3Mo_3N, ***Journal of Phys. Chem. C, 2018***, *122, 6078*

ACKNOWLEDGEMENTS

Andy Logsdail, Stefan Nastase , Justin Hargreaves, Michael Higham, David Jurado, David Santos-Carballal, Constantinos Zeinalipour-Yazdi, Graham Hutchings, Alberto Roldan, Nora de Leeuw, Alexei Sokol, Russell Howe, Santosh Matam, Alex O'Malley, Stewart Parker.

EPSRC, GCRF, and Johnson Matthey - *funding*

CatalysisHub

Announcements

ugm.materialsdesign.com

Dr. Erich Wimmer

Materials Design

Professor Chris Van der Walle

University of California Santa Barbara

Dr. Jörg-Rüdiger Hill

Materials Design

Dr. Marianna Yiannourakou

Materials Design

Next Week's Interview

October 14th

Next Week's MedeA Training

October 12th

Question and Answer Session

Dr. Clive Freeman

Materials Design

Professor Sir Richard Catlow

University College London

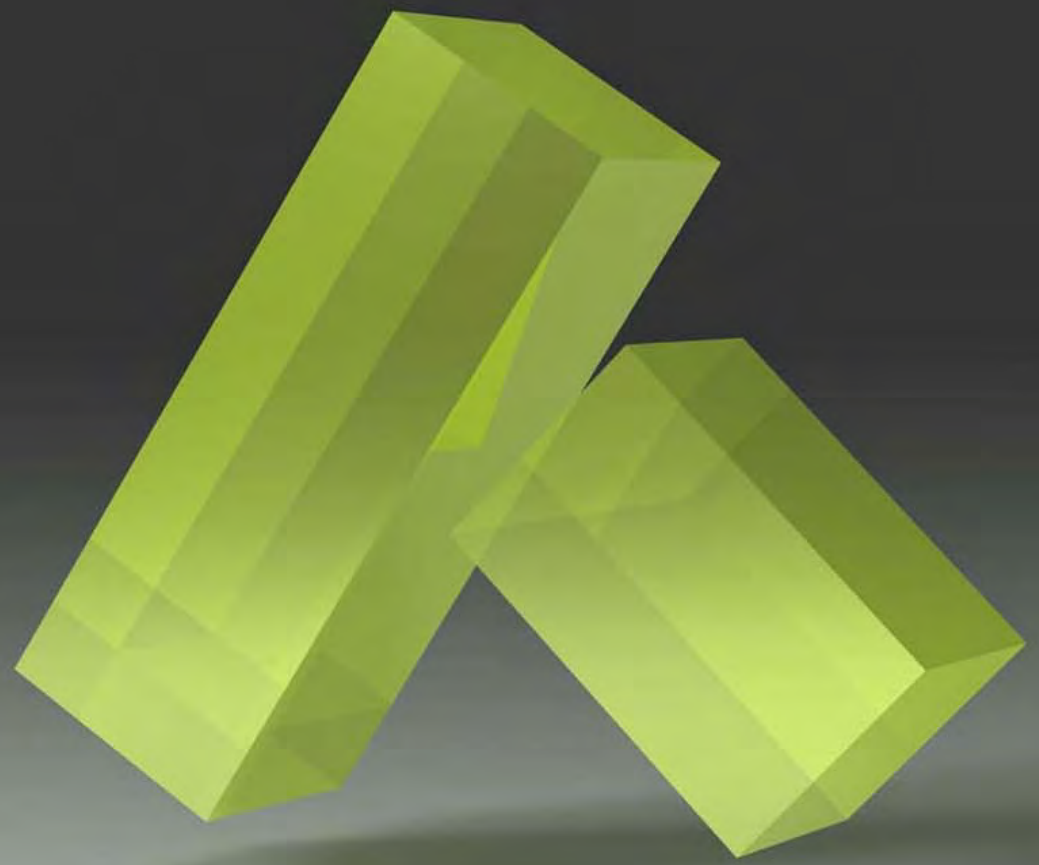
Questions about Materials Design UGM

ugm@materialsdesign.com

materials design

info@materialsdesign.com

www.materialsdesign.com



MedeA

Innovation by Simulation