Supplementary Information for:

Integrated theoretical and empirical studies for probing substrate-framework interactions in hierarchical catalysts

Stephanie Chapman,[a] Alexander J. O'Malley,[b, c, d] Ivana Miletto,[e] Marina Carravetta,[a] Paul Cox,[f] Enrica Gianotti,[e] Leonardo Marchese,[e] Stewart F. Parker,[b, g] Robert Raja.[a]

a) Department of Chemistry, University of Southampton, University Road, Southampton SO17 1BJ, U.K.
b) UK Catalysis Hub, Research Complex at Harwell, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, OXON, OX11 0QX, U.K.
c) Centre for Sustainable Chemical Technologies (CSCT), Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, U.K.
d) Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, U.K.
e) Department of Science and Technological Innovation, Università del Piemonte Orientale, Viale T. Michel 11, 15121 Alessandria, Italy.
f) School of Pharmacy and Biomedical Sciences and Institute of Biomedical and Biomolecular Sciences, University of Portsmouth, Portsmouth, PO1 2DT, U.K.
g) ISIS Pulsed Neutron and Muon Facility, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, OXON, OX11 0QX, U.K.

Contents

Powder X-ray diffraction data

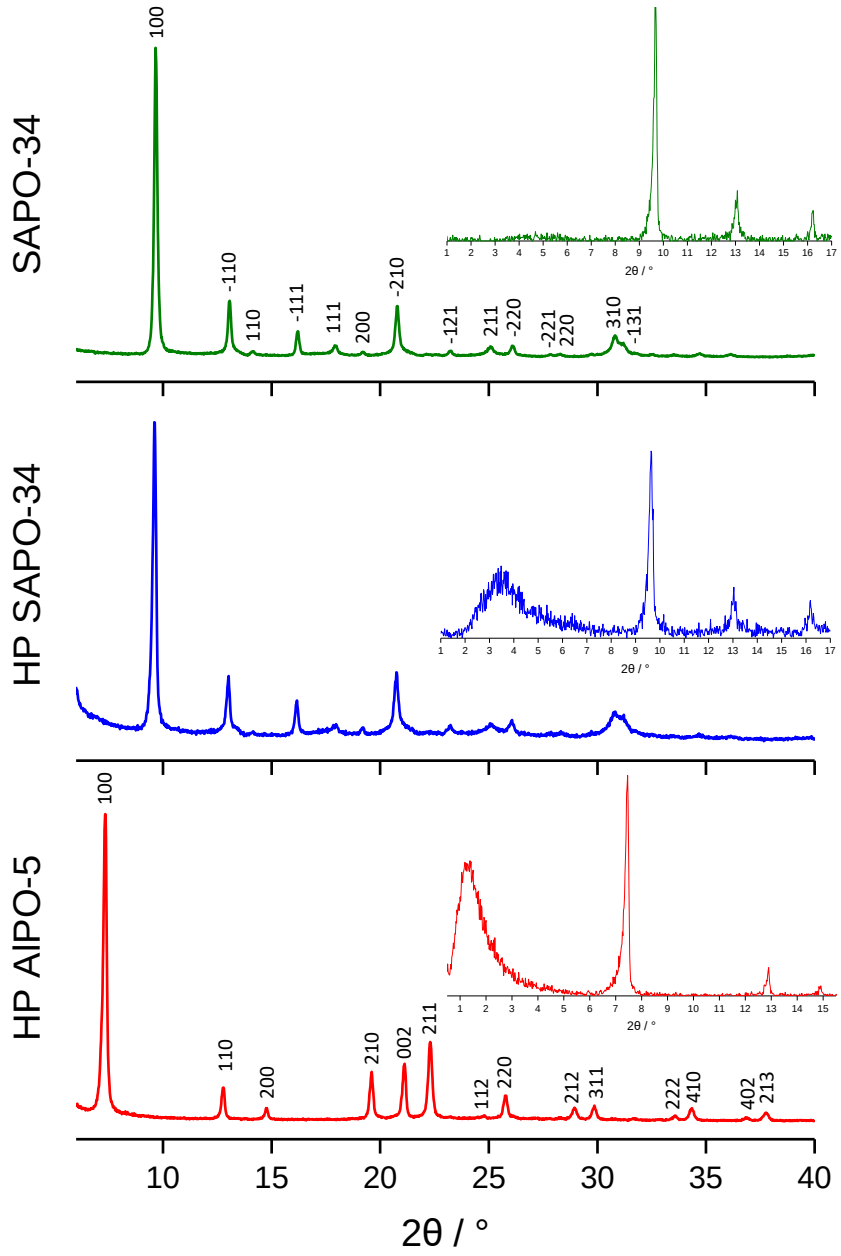

Figure S1: Indexed powder XRD pattern of SAPO-34 (top, green), HP SAPO-34 (middle, blue) and HP AlPO-5 (bottom, red), with their respective low-angle spectra inset.

Table S1: The experimental unit cell parameters for SAPO-34, HP SAPO-34 and HP AlPO-5 catalysts, with refinements performed using the CelRef software.[1]

Catalyst	Lattice Parameters				Space Group	Unit Cell Volume / Å^3
	***a* = *b* / Å**	***c* / Å**	**α = β / °**	**ϒ / °**		
SAPO-34	13.62	14.85	90	120	R-3m	2385
HP SAPO-34	13.64	14.85	90	120	R-3m	2393
HP AlPO-5	13.81	8.40	90	120	P6cc	1389

BET gas physisorption data

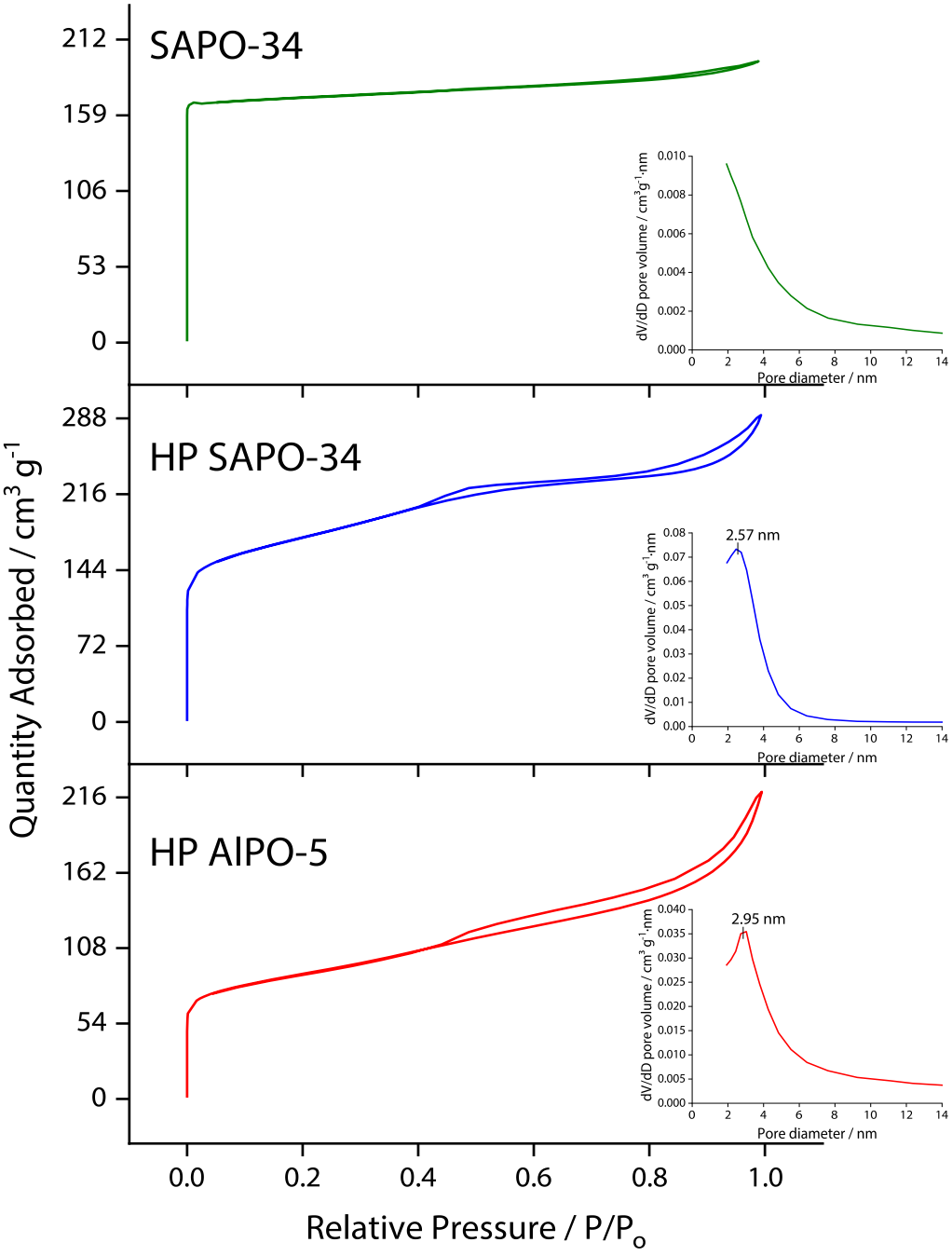

Figure S2: N_2 gas adsorption/desorption isotherm of SAPO-34 (top, green), HP SAPO-34 (middle, blue) and HP AlPO-5 (bottom, red) at 77K, with their respective BJH pore-size distribution inset.

Table S2: Textural properties of SAPO-34, HP SAPO-34 and HP AlPO-5 catalysts determined by N_2 adsorption/desorption studies.

Catalyst	S_{BET} / m^2 g^{-1}	V_{micro} / cm^3 g^{-1}	V_{meso} / cm^3 g^{-1}	External surface area / m^2 g^{-1}	Mesopore diameter / Å
SAPO-34	548	0.24	-	49	-
HP SAPO-34	589	0.13	0.14	319	26
HP AlPO-5	323	0.06	0.20	180	30

FT-IR spectra of catalysts

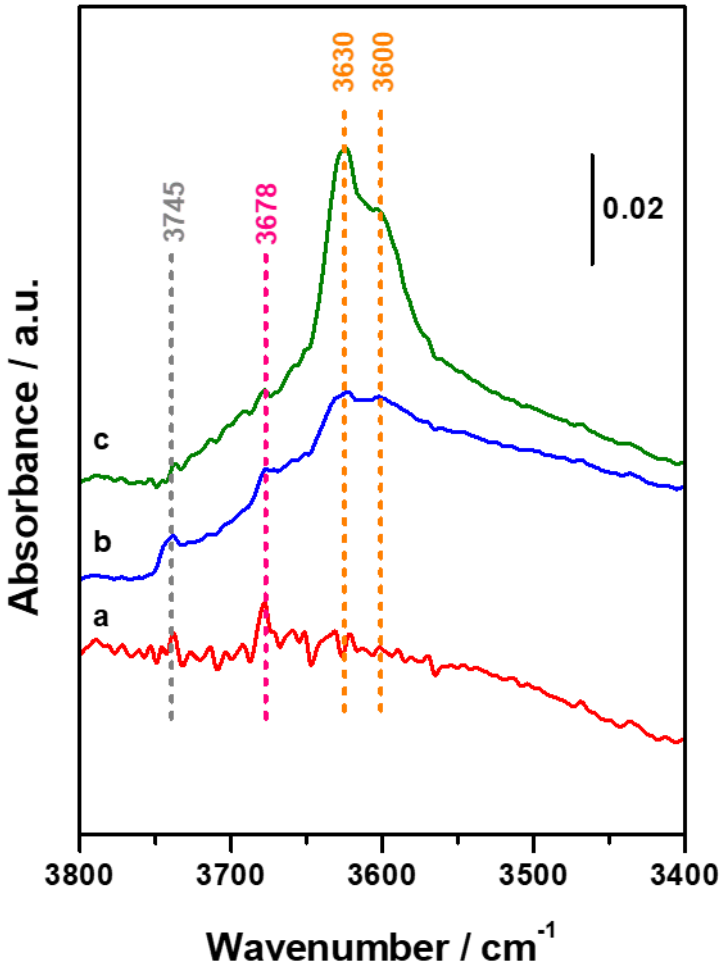

Figure S3: FTIR absorbance spectra in the O-H stretching region of HP AlPO-5 (curve a, red), HP SAPO-34 (curve b, blue) and SAPO-34 (curve c, green) with modes associated with Brønsted acid sites (orange), P-OH sites (pink) and Si-OH (grey) labelled.

Solid-state NMR spectrum of cyclohexanone oxime

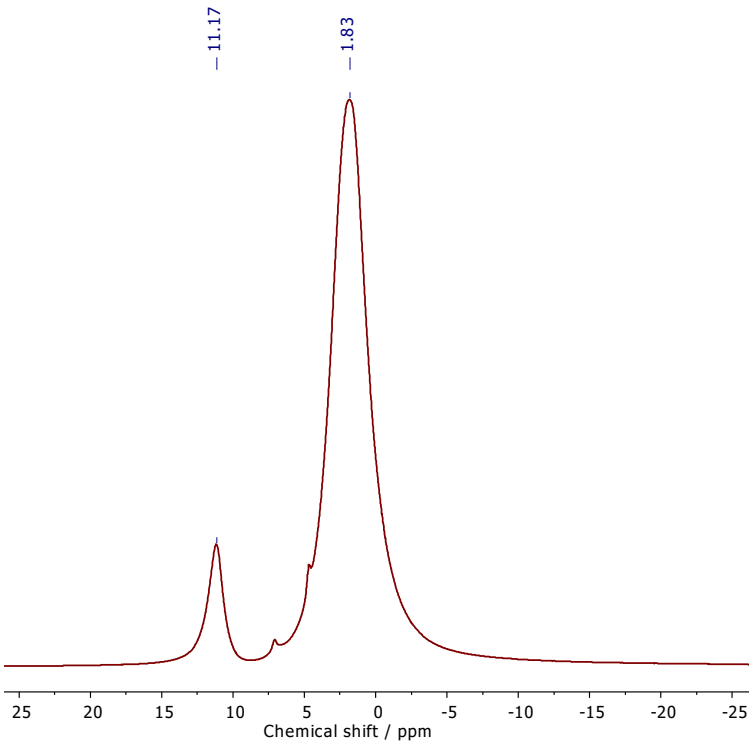

Figure S4: ^{1}H MAS NMR spectrum of cyclohexanone oxime acquired at 600 MHz and a spinning frequency of 27 kHz.

References:

1. Laugier, J.; Bochu, B. CelRef Version 3. http://www.ccp14.ac.uk/tutorial/lmgp/celref.htm.