

Heterogenized ionic liquid-metal oxide hybrids: enhanced catalytic activity in the liquid-phase Beckmann rearrangement

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7 Heterogenized ionic-liquid metal-oxide hybrids:
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11 enhanced catalytic activity in the liquid-phase
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15 Beckmann rearrangement
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40 **ABSTRACT**
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44 We report the design of stable, ionic liquid-hybrids, covalently-anchored to the framework
45 architectures of microporous and hierarchical solid supports. The ionic liquid moieties that are
46 anchored to the framework facilitate enhanced mass-transport, and afford superior catalytic
47 performance in the Beckmann rearrangement of cyclic oximes at low-temperatures. The ionic
48 liquid-metal oxide (IL-MO) hybrids also play an important role in modifying the reaction pathway
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3 and synergistic enhancements in catalytic properties are attributed to the increased hydrophobicity
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5 of the anchored, imidazolium-based ionic liquid.
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9 **KEYWORDS:** Ionic liquid hybrids, Hydrophobic surface, Hierarchical oxides, Beckmann
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11 rearrangement, Caprolactam.
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14 15 16 17 18 **INTRODUCTION**

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21 The design of functional, inorganic–organic hybrid catalysts is emerging as an effective route to
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23 resolve some of the challenges facing process chemistry, including the sustainable production of
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25 bulk and fine chemicals.¹ The synergic effect of both inorganic and organic moieties in these
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27 hybrid materials leads to remarkable improvements in catalytic performance in many applications,
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29 including acid-base catalysis, chiral transformations, polymerization and selective oxidation.
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31 Catalytic reactions that have benefited from this approach include *trans*-esterification,²
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33 Knoevenagel condensation,³ Sonogashira coupling,⁴ the synthesis of cyclic carbonates from CO₂
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35 and epoxide,⁵ asymmetric epoxidation,⁶ hydrogenation,⁷ ethylene polymerization,⁸ dehydration,⁹
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37 and the selective oxidation of sulfides and alcohols.¹⁰ However, whilst catalytically efficient, the
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39 instability of many of these hybrid materials limits their widespread application.
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45 More recently, hybrid materials created by incorporating ionic liquids (ILs) into solid-oxides
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47 have attracted increasing interest, owing to their relatively high boiling point, low vapor pressure,
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49 high thermal and chemical stability, and versatile functionality.¹¹ Different classes of ILs,
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51 including task-specific ILs (TSIL) and Brønsted-acidic ILs (BAIL), have been employed in
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53 catalysis, extraction, chemical analyses and other industrial applications.¹² For example, Visser *et*
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55 *al.* reported a series of hydrophobic TSILs that can be used to extract toxic, heavy-metal cations
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3 from water. These TSILs, containing a urea-, thiourea-, or thioether-substituted alkylimidazolium
4 cation with the $[\text{PF}_6]^-$ anion, were found to selectively coordinate Hg^{2+} and Cd^{2+} ions.¹³ Hybrid
5 materials of ILs, including poly(ionic liquid)s (PILs) and IL-silica gels (sometimes referred to as
6 ionogels), have found extensive application as catalysts for many organic transformations.^{14, 15}
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8 Recently, we reported the preparation of a stable IL gel (a hybrid of silica and a functionalized
9 acidic IL, triethylammonium propanesulfonate bistriflimide) that exhibits superior catalytic
10 performance in the dehydration of *rac*-1-phenyl ethanol.¹⁶
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19 Supported ionic liquid phases (SILPs), in which a thin layer of IL is deposited on to a supporting
20 matrix, have also emerged as promising candidates in the last few years and are of considerable
21 interest as functional catalysts and adsorbents.^{17,18} However, the stability of SILPs is a concern, as
22 leaching of the ionic liquid moiety from the inorganic oxide surface can impact their recyclability,
23 particularly in liquid phase reactions.¹⁹ To address the issue of leaching, covalent anchoring has
24 been used to chemically attach ILs to a matrix - for example *via* bonds to surface hydroxyl groups
25 on a metal-oxide support.²⁰ Additionally, to overcome the diffusion limitations of microporous
26 supports employed, such as zeolites and aluminophosphates, hierarchically-porous (HP) zeolite
27 and oxide analogues have been developed.²¹⁻²³ These HP materials are characterized by having
28 multiple levels of porosity (including micro- (< 2 nm), meso- (2-50 nm) and/or macro- (> 50 nm)
29 pores). Micro-meso zeolites, for example, can advantageously combine the catalytic features of
30 the microporous parent framework with the improved access and transport properties associated
31 with the mesoporous network.²⁴ Therefore, as well as overcoming diffusion limitations, HP
32 materials broaden substrate scope by accommodating larger reactants, expanding the range of
33 catalytic applications.²⁵
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3 Given our interest in developing sustainable methodologies using a green chemistry approach,
4 we have investigated the conventional homogeneous process to produce cyclic lactams, which are
5 important feedstocks in the polymer industry. The Beckmann rearrangement (BR) of cyclic oximes
6 to their corresponding lactam, is conventionally achieved using a mineral acid catalyst (typically
7 sulfuric acid or oleum).²⁶ However, the use of such mineral acid catalysts necessitates a
8 neutralization step that is detrimental to the atom efficiency of the process. As such, there has been
9 considerable interest in designing heterogeneous catalysts for the industrial BR,^{27,28} as reflected in
10 the diversity of research publications and patents describing solid-acid catalysts (including
11 zeolites,²⁹⁻³³ metal-modified zeolites,³⁴⁻³⁸ mesoporous silica,³⁹⁻⁴¹ SAPOs,^{38,42,43} metal oxides or
12 supported metal oxides⁴⁴⁻⁵¹ that operate under vapor-phase conditions (≥ 300 °C). However, many
13 of these solid-acid BR catalysts have low selectivity towards the desired lactam product and
14 experience relatively fast deactivation due to the high temperatures employed.⁵² The presence of
15 active sites such as terminal silanol groups and strong Brønsted acidic sites has been identified as
16 detrimental to catalytic performance using these solid catalysts.^{48,49,52} Many researchers have
17 attempted to incorporate suitable modifiers or diluents to the heterogeneous BR catalysts and/or
18 processes to mitigate, or limit, the role of stronger acid sites. One such modification was the
19 continuous addition of methanol,²⁷ which caps terminal silanol sites with the methoxy moiety.
20 Whilst effective, the use of methanol necessitates additional processing steps, leading to increased
21 costs and reduced efficiency. Furthermore, even though a continuous catalytic process is
22 advantageous in many aspects, coking and fast deactivation of solid catalysts, rigorous reaction
23 conditions, and a high energy input, warrants research into more sustainable liquid-phase
24 conditions.⁵³⁻⁵⁶ Hence it is desirable to design efficient, solid-acid catalysts that can operate under
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3 the conditions of the liquid-phase BR (LBR), to mitigate the formation of condensation by-
4 products.^{56,57}
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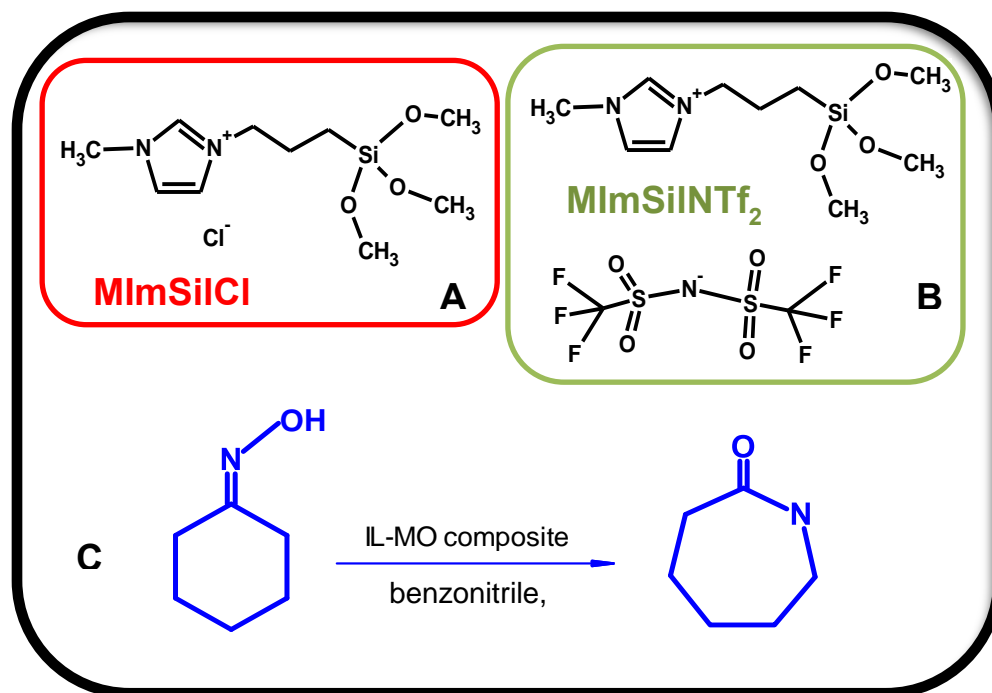
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8 The advantages of ILs in the liquid-phase Beckmann rearrangement (LBR), either as the reaction
9 medium, or as additives to improve the water tolerance of Lewis acids, is known.⁵⁸⁻⁶⁰ For example,
10 the hydrophobicity and water-immiscibility of a TSIL comprising the ethylimidazolium cation
11 with sulfonyl chloride, and PF_6^- as anion, has been exploited in the water-assisted extraction of
12 caprolactam (CL) from the BR reaction mixture.⁶¹ Moreover, when metaboric acid was used as a
13 catalyst in an IL reaction medium,⁶² the acidity of metaboric acid, combined with the hydrophobic
14 nature of the IL, was found to achieve better conversion of oximes in the LBR.
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24 When Karimi *et al.* confined the relatively hydrophobic IL, 1-methyl-3-octylimidazolium
25 hydrogen sulfate ($[\text{MOCIm}]\text{HSO}_4$), inside the meso-channels of SBA-15-functionalized
26 propylsulfonic acid, the SBA-15 hybrid exhibited higher catalytic performance than the bare
27 support in esterification reactions.⁶³ The superior activity was explained on the basis of the
28 hydrophobic nature of the *n*-octyl substituent of the IL, which, by repelling water from the catalyst
29 surface and inhibiting the diffusion of water into the pores, improved the accessibility of the active
30 sites for organic substrates.
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40 Herein, we present an interesting synergism of IL ions supported on microporous and
41 hierarchical architectures, for the LBR of cyclohexanone oxime (Scheme 1) inspired by the
42 attenuating affect achieved by co-feeding methanol into the fluidized bed reactor of the
43 commercial MFI catalyst.²⁷ It was proposed that the methanol reacts selectively with the terminal
44 silanols of the zeolite to form methoxy groups, thereby minimizing side reactions. The zeolite
45 powder in the fluidized bed reactor is continuously regenerated and methanol is recycled during
46 this process. Thus, we proposed that, by covalent anchoring of stable ions derived from an IL, we
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3 could achieve permanent capping of unwanted hydroxyls present in the catalysts. By immobilizing
4 the IL *via* alkoxy silane groups to surface hydroxyl groups of the support material, it has been
5 possible to create stable, composite catalysts with enhanced hydrophobicity around the active site.
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10 The result is a robust IL-MO hybrid exhibiting improved yield of CL in the LBR.
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Scheme 1. The structure of the ionic liquids MImSiCl (A) and MImSiNTf₂ (B) with alkoxy silane groups (prior to anchoring), and a scheme for the Beckmann rearrangement, catalyzed by an ionic liquid-metal oxide (IL-MO) hybrid catalyst (C).

EXPERIMENTAL

Synthesis of hierarchically-porous supports and IL hybrids.

HP AIPO-5: The synthesis of hierarchically-porous aluminophosphate-5 (HP AIPO-5) was carried out as previously reported in the literature.²³ Phosphoric acid (4.6 mL, 85 wt. % in H₂O, Sigma Aldrich) was mixed with distilled water (20 mL) in a Teflon beaker. Aluminium isopropoxide (13.6 g, Sigma Aldrich) was slowly added to the solution and vigorously stirred for 1.5 hours until a homogeneous solution was formed. Dimethyloctadecyl 3-(trimethoxysilyl)propyl ammonium chloride (DMOD, 2.4 mL, 72 wt. % in H₂O, Sigma Aldrich) was added dropwise,

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3 followed by triethylamine (7.4 mL, Sigma Aldrich), also dropwise. Distilled water (40 mL) was
4 added, and the resulting white slurry stirred for 1 hour. The gel was transferred to a Teflon-lined,
5 stainless-steel autoclave and crystallized under hydrothermal conditions in a heated fan-assisted
6 oven (WF-30 Lenton) at 200 °C for 24 hours. The solid product was collected *via* vacuum filtration
7 and washed with deionized water (500 mL). The product was dried overnight in an oven at 80 °C.
8 The as-synthesized catalyst was calcined in a tube furnace under a flow of air at 600 °C (3 °C min-
9 1 ramp rate) for 16 hours, yielding a white powder of HP AlPO-5.

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19 **HP ZSM-5:** The ammonium form of the commercial HZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$, Alfa
20 Aesar) was converted to its protonic form by heating in a tube furnace at 550 °C for 5 hours, under
21 constant air flow. Desilication was carried out using an established protocol.²⁵ ZSM-5 powder (5
22 g) was transferred to a round-bottom flask (RBF) containing hot (65 °C) aqueous NaOH solution
23 (250 mL, 0.2 M). With a water cooled condenser, the reaction was stirred constantly at 65 °C for
24 2 hours. The reaction was quenched in an ice bath before centrifugation, washing thoroughly with
25 deionized water until at pH 7. The material was dried overnight in an oven at 80 °C. The resulting
26 solid was transferred to a RBF containing aqueous solution of NH_4OH (50 mL solution per 0.5 g
27 powder, 0.5 M) and then stirred under reflux (80 °C) for 4 hours. The reaction was cooled, and the
28 solid collected by centrifugation was washed with deionized water. The solid was dried overnight
29 in an oven at 80 °C, before calcination in a tube furnace, under a flow of air, at 550 °C for 5 hours.

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45 Synthetic procedures for the preparation of microporous supports and ILs are reported in the
46 Supporting Information (SI).

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49 **Procedure for grafting IL on to support oxide:** The covalent anchoring of ionic liquid to the
50 support materials was achieved following the reported protocol.⁶⁴ The dried support (1 g) was
51 transferred to a RBF containing dry toluene (50 mL, Sigma Aldrich). The IL (0.5 mmol) was added
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3 to the RBF, which was refluxed for 20 hours under constant stirring. The reaction mixture was
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5 cooled to room temperature, and the solid collected by vacuum filtration. Unreacted IL was
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7 removed by soxhlet extraction with dichloromethane solvent. The resulting IL-MO hybrid
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9 materials were first dried in low vacuum, and then at 90 °C with high vacuum on a Schleck line.
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12 **Procedure for the liquid phase Beckman rearrangement:** Cyclohexanone oxime (0.1 g,
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14 Sigma Aldrich), molar ratio of ionic liquid to oxime 0.05:1, anhydrous benzonitrile (20 mL, Sigma
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16 Aldrich), and the internal standard, anhydrous chlorobenzene (0.1 g, Sigma Aldrich) were added
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18 to a three-necked RBF fitted with a reflux condenser, stopper, and rubber septum. Under constant
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20 nitrogen atmosphere, the reaction was heated to 130 °C under stirring. The reaction was monitored
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22 by sampling on an hourly basis, and analyzed by gas chromatography using a Perkin Elmer GC
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24 Clarus 480 with capillary column and flame-ionization detector (FID). Reagents and products were
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26 quantified against the internal standard, chlorobenzene.
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33 **RESULTS AND DISCUSSION**

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35 In the following discussion, microporous and hierarchically-porous (HP) analogues of the
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37 aluminosilicate, H-ZSM-5 (MFI), and the aluminophosphate, AlPO-5 (AFI), are used as support
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39 materials. Herein, these frameworks are designated AlPO-5, HP AlPO-5, H-ZSM-5, and HP ZSM-
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41 5. Whilst a soft, dual-templating (bottom-up) approach was used to introduce hierarchical porosity
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43 into AlPO-5, the hierarchical H-ZSM-5 was formed by post-synthetic desilication (a top-down
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45 approach).^{23,25} One of two imidazolium ILs, 1-methyl-3-(propyltrimethoxysilane)imidazolium
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47 chloride (MImSilCl) or 1-methyl-3-(propyltrimethoxysilane)-imidazolium bistriflimide
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49 (MImSiINTf₂), was covalently anchored to the framework *via* the alkoxy silane group.
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To ensure the phase purity of the parent oxide and hybrid materials, a powder X-ray diffraction (PXRD) pattern of each material was acquired (Figure 1). The PXRD pattern of microporous and hierarchical AlPO-5 and H-ZSM-5 were correlated with the AFI- and MFI-type frameworks, respectively, confirming their phase purity.^{23,25} Encouragingly, the PXRD profiles of the supports was unchanged after covalent anchoring of the IL ions, indicating that their crystalline structure was not disrupted by the tethering process.

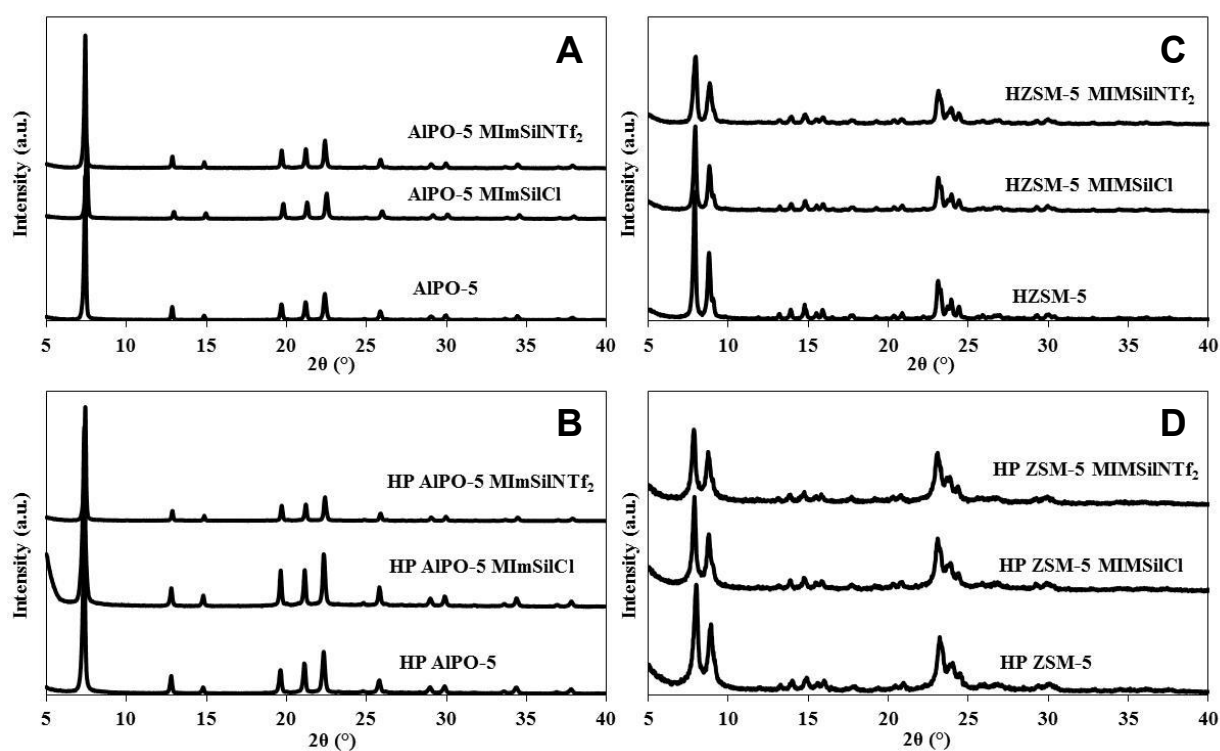


Figure 1. The PXRD profiles of the parent oxide and covalently-anchored IL-MO hybrids of AlPO-5 (A), HP AlPO-5 (B), and HZSM-5 (C) and HP ZSM-5 (D).

To assess whether the covalent anchoring of IL ions was successful, the surface area (SA) and pore volume (PV) of the hybrids were compared to the parent oxide using the N₂ adsorption-desorption technique (Table S1). Both microporous AFI and MFI frameworks were found to have

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3 a Brunauer-Emmett-Teller (BET) surface area and pore volume consistent with that reported in
4 literature,^{23,25} but the SA and PV were enhanced in their HP analogues. Higher SA and pore sizes
5 were observed with the HP ZSM-5 material that was prepared by desilication methodology, in line
6 with reported observations.²⁵ The SA and PV of all parent oxides were significantly decreased
7 after covalent-anchoring of the ILs, indicating the formation of hybrid materials. The most
8 accessible binding points are likely to be hydroxyl groups on the surface and at the pore-mouths
9 of the support.⁶⁵

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11 The N₂ adsorption-desorption isotherms of HP AlPO-5, microporous H-ZSM-5 and their IL
12 hybrids are given in Figure 2 (AlPO-5 and HP ZSM-5 in Figure S1). Both hierarchical oxides and
13 their corresponding hybrids exhibit Type IV isotherms, with hysteresis loops that are indicative of
14 mesoporosity.⁶⁶ Whilst the microporous AFI and MFI materials also exhibit some hysteresis, this
15 is attributed to inter-crystalline mesoporosity. Moreover, while AlPO-5, HP AlPO-5 and HZSM-
16 5 possess H4-type hysteresis, HP ZSM-5 exhibits H3 hysteresis due to the presence of larger
17 mesopores after desilication. Although the structures of the isotherm and hysteresis loops are
18 unchanged by tethering, the adsorption capacity of the support is significantly decreased;
19 particularly in the case of the AFI materials, which are essentially non-porous. The pore size
20 distribution indicates that IL-anchoring causes a uniform decrease of pore volume across the range
21 of pore diameters, supporting the PV data (Table S1). As well as textural analyses, the successful
22 covalent anchoring of IL in these hybrid materials is evidenced by C, H and N elemental analysis
23 (Table S1), which shows these elements to be present in quantities that correlate with the amount
24 of IL used in tethering.

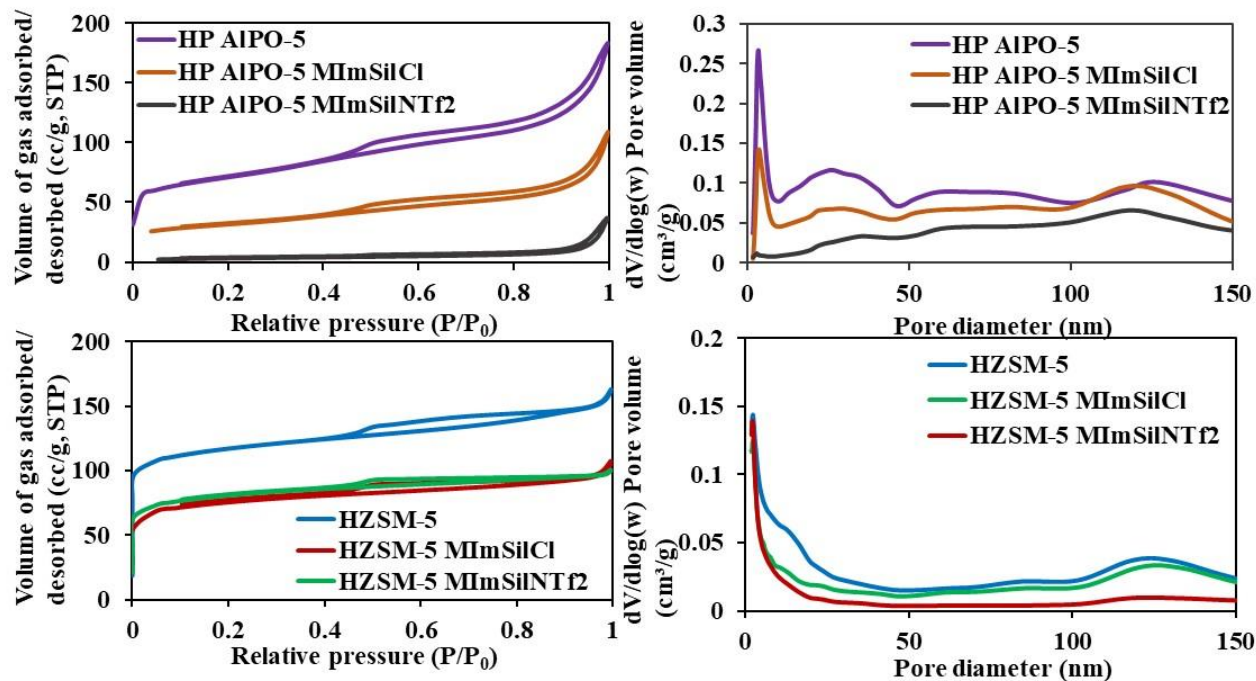


Figure 2. N₂ adsorption-desorption isotherms (left) and pore size distributions (right) of the parent oxides HP AlPO-5 (top) and H-ZSM-5 (bottom) and their IL-MO hybrids.

The integrity of the anchored IL ions was evidenced by magic-angle spinning nuclear magnetic resonance (MAS NMR) studies. The covalent linkage between the silane of the IL and the support was evidence by ²⁹Si NMR (Figure S2) as a broad signal centered at -62 ppm, which is consistent with Si-C covalent bonding. The breadth of the peak is attributed to the different modes of binding: XSi(OSi)₃, XSi(OSi)₂OR and XSi(OSi)(OR)₂. Distinct peaks at -56 and -67 ppm, corresponding to T² XSi(OSi)₂(OR) and T³ XSi(OSi)₃, respectively, reveal preferred binding modes. In addition, peaks corresponding to tetrahedral silicon atoms were identified in HP AlPO-5. A broad signal observed between -90 to -110 ppm (encompassing Q² (Si(OH)₂(OSi)₂), Q³ (Si(OH)(OSi)₃) and Q⁴ (Si(OSi)₄ species) derives from the siliceous surfactant template, where the alkoxy silane component becomes integrated into the mesopore walls.⁶⁷ The presence of tethered IL on the solid

oxide surface was also confirmed by ^{13}C MAS NMR (Figure S2). Peaks corresponding to SiCH_2 , $-\text{CH}_2$, N-CH_2 and N-CH_3 (methyl imidazole) are observed at 9.4, 23.5, 51.9 and 36.6 ppm, respectively, and resonances at 123.5, 128.2 and 136.8 ppm are attributed to the ring-carbon atoms of imidazole.⁶⁸ Additionally, infrared (IR) spectroscopy (Figure S4 and S5) confirmed that the integrity of the IL was retained when it was anchored to the oxide supports (C-H stretching bands of the C-H in imidazolium ring and chain of IL at 3165, 3127, 2991 and 2958 cm^{-1}).⁵

The thermal stability of the hybrid materials was assessed by thermogravimetric analysis (Figure S3). Due to the covalent anchoring strategy, the hybrids were found to be stable up to ~ 350 °C, although the weight loss pattern was dependent on the IL, and also on the pore size of the parent oxide. In general, the MImSiCl-based composites exhibit two distinct weight loss regions at ~ 230 °C and another after 430 °C, whereas the MImSiNTf₂-based hybrids possess a single, distinct weight loss > 350 °C. Also, the more hydrophobic hybrid materials, with the bulky bistriflimide anion, have a greater thermal stability than their chloride-anion analogues. This phenomenon has previously been reported,⁶⁹ and arises where the diffuse and delocalized charge on the NTf₂⁻ anion decreases interaction with cations, increasing IL stability relative to the more localized charge of the hydrophilic halides.⁷⁰

The catalytic activity of the IL-MO hybrids was assessed in the liquid-phase Beckmann rearrangement (LBR) at 130 °C, using benzonitrile as solvent. The catalytic results (% yield of caprolactam obtained after 6 hours of reaction) are presented in Figure 3, and details of the % conversion of cyclohexanone oxime, % selectivity to caprolactam (CL), and the % yield of CL can be found in Table S2.

As reported in literature, the catalytic activity of HZSM-5 frameworks is derived from the weakly-acidic hydroxyl groups present on the surface.²⁷ It was reported that the acidic properties

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3 of the hydroxyl groups present inside the pore structure (i.e. defect silanols or nest silanols) are
4 responsible for the activation of oxime molecules, while the terminal silanols are responsible for
5 hydrolysis of oxime to the ketone by-product.^{27,56} In contrast, the catalytic activity of HP AlPO-5
6 is derived mainly from the pendant silanol groups present in the mesopores (originating from the
7 surfactant template), with some contribution from Al-OH and P-OH defect sites.²³

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10 Firstly, there is a significant enhancement in CL yield at 6 hours for the HP oxides *versus* their
11 microporous counterpart. It should be noted that the siliceous surfactant employed for the
12 preparation of HP AlPO-5 materials, results in the formation of silanol groups in the mesopores
13 that, upon calcination, are available for catalysis.²³ As a result of the increased number of active
14 sites (i.e. silanol sites) and the increased pore volume and pore size, CL yield is approximately
15 doubled in HP AlPO-5, compared to its microporous counterpart.^{23,25} Likewise, the CL yield
16 obtained with HP ZSM-5 (60 %) exceeds that of its microporous HZSM-5 analogue (22.6 %). A
17 similar observation was reported earlier by Gianotti *et al.*, who prepared hierarchical HZSM-5
18 with accessible active sites using a desilication methodology.²⁵ The interplay between the
19 enhanced accessibility of acid sites, coupled with the secondary porosity in HP ZSM-5 enhances
20 both the oxime conversion and the lactam selectivity. The very high yield of CL in the case of HP
21 ZSM-5 oxide can be attributed to its high mesopore volume and pore size, which are evident from
22 the BET and textural properties. These mesopores and accessible silanols assist the uninterrupted
23 CL desorption from the active sites and easy diffusion of reactant and product through the porous
24 structure.

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27 The anchored ILs have a marked influence on the catalytic performance in the LBR (Figure 3).
28 Magic-angle spinning nuclear magnetic resonance (MAS NMR) characterization has shown that
29 the methoxy silane groups of the ILs interact with the hydroxyl groups of the framework, leading
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3 to covalent tethering of the IL ions to the oxide. A separate study is currently being undertaken in
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5 order to establish whether the IL groups are anchored to the oxide surface, or to accessible
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7 hydroxyls inside the mesoporous structure. Interestingly, the two ILs, albeit closely-related in
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9 structure (having the same cation, methyl(3-propyltrimethoxysilane)imidazolium, but different
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11 anions), elicit different behavior in the BR of cyclohexanone oxime. The more hydrophilic,
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13 chloride-containing IL, MImSiCl, causes a decrease in yield of CL, which is most pronounced for
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15 the microporous frameworks. In contrast, the more hydrophobic MImSiNTf₂ IL increases the
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17 performance significantly when anchored to microporous and HP AlPO-5, and microporous H-
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19 ZSM-5. The implication is that hydrophilic groups have an adverse influence on the BR,
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21 encouraging water molecules (that originate from the reaction, or introduced with the IL) to
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23 interact with, or be retained at polar domains, such as the active sites. However, with a more
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25 hydrophobic moiety, water is discouraged near the active site, and hence the catalytic performance
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27 of the oxides is enhanced by the presence of ions derived from MImSiNTf₂. Catalytic performance
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29 was most significantly increased when MImSiNTf₂ was anchored to the HP AlPO-5 material. In
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31 this case, the enhancement in catalytic performance is believed to be a combination of the
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33 hierarchical porosity, the nature of the active sites, and the enhanced hydrophobicity, which
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35 facilitate the rearrangement of cyclohexanone oxime to caprolactam, as depicted in Scheme S1.
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37 We believe that the anchored ionic liquid modifies the immediate chemical environment near the
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39 active site (silanols), which not only accelerates the Beckmann rearrangement, but also enhances
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41 catalyst selectivity by excluding the water by-product that is generated during the reaction.
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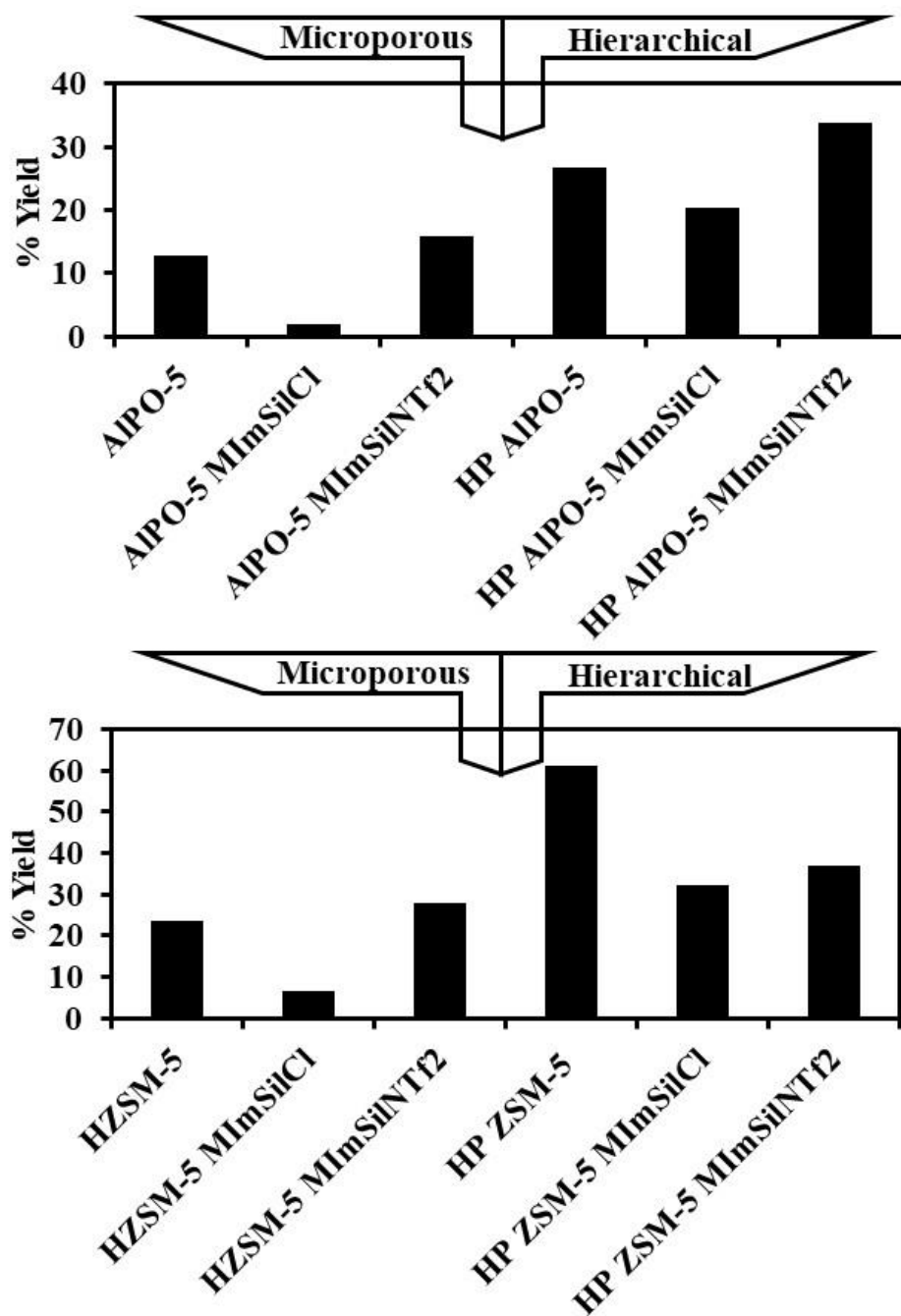


Figure 3. The % yield of caprolactam in the liquid-phase Beckmann rearrangement of cyclohexanone oxime using AFI-based materials (top) and MFI-based materials (bottom). Reaction conditions: cyclohexanone oxime (0.1 g), chlorobenzene (0.1 g, internal standard), molar ratio of ionic liquid to oxime 0.05:1, benzonitrile (20 mL, solvent), at 130 °C for 6 hours.

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3 In contrast to HZSM-5, HP ZSM-5 materials were found to operate best without modification.
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5 In line with earlier observations, the hydrophobic MImSiINTf₂ variant in HZMS-5 and HPZSM-5
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7 affords superior catalytic performance when compared with the hydrophilic MImSiCl analogue.
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10 More importantly, the catalytic activity of HP ZSM-5 is influenced primarily by the accessible
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12 acid sites and hierarchical porosity; and the hydrophilic/hydrophobic properties of the IL are not
13
14 the principal determinant, when compared with the HP AlPO-5 framework. Hence, further surface
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16 modification studies using organosilane were undertaken in order to probe the effect of
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18 hydrophobicity on the HZSM-5 and HP AlPO-5 supports.
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21 The enhanced hydrophobicity of HP AlPO-5 MImSiINTf₂ is evidenced by the contact angle and
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23 the shape of the water drops on the surface of this hybrid. Whilst water forms a spherical droplet
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25 on the surface of the HP AlPO-5 MImSiINTf₂ hybrid wafer (contact angle 58.4 °), it adheres to
26
27 the surface of the chloride counterpart (contact angle ~ 0 °), and also the bare oxide (Figure 4). In
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29 addition, when IL-MO powders were combined with a water/*n*-hexane mixture, the more
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31 hydrophobic HP AlPO-5 MImSIINTf₂ was found to interact with the oil layer, whereas the parent
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33 framework and the chloride-IL hybrid counterpart preferentially interacted with the water layer
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35 (Figure S8).
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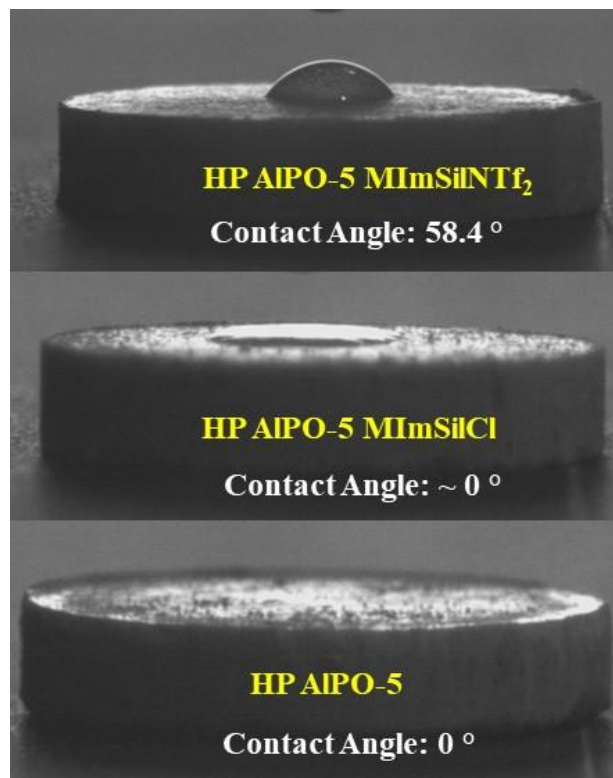


Figure 4. Images of the contact angle made by a water droplet on a wafer of HP AlPO-5 and its IL-hybrids.

To further substantiate the importance of hydrophobicity in the catalytic LBR, HZSM-5 and HP AlPO-5 supports were modified with a long chain organosilane, hexadecyltrimethoxysilane (HDS), adopting an analogous procedure to that employed for the preparation of IL-MO hybrids. The covalent anchoring of the silane was evidenced by gas adsorption studies and elemental analyses (Figure S9 and Table S3). It was proposed that, if the improved performance of the MImSiINTf₂ hybrid material was due to increased hydrophobic character, similar enhancements might be achieved using the HDS-hydrophobized supports. However, it was found that the catalytic performance of the hydrophobic hybrids was significantly lower than the hydrophobic IL-MO hybrids (Figure 5). Interestingly, this contrasts with the results of Xu *et al.* who modified

the surface of ZSM-5 with organosilane molecules of varying chain length to create hydrophobic materials with superior activity in catalytic dehydration.⁷¹ In their study, the HDS was grafted to external silanols on ZSM-5, leading to a marked increase in contact angle of water droplet (from 15 ° on the unmodified material, to 134 ° after surface modification).⁷¹ In our case, despite modifying the surface of the support materials with long chain silanes, the resulting hybrids did not exhibit the improved catalytic activity that might be expected on the basis of results obtained with the IL-MO hybrids. These findings give support to the theory that the unique catalytic properties of IL-MO hybrids arise as a result of the IL selectively modifying some of the undesired active sites present on the oxide surface.

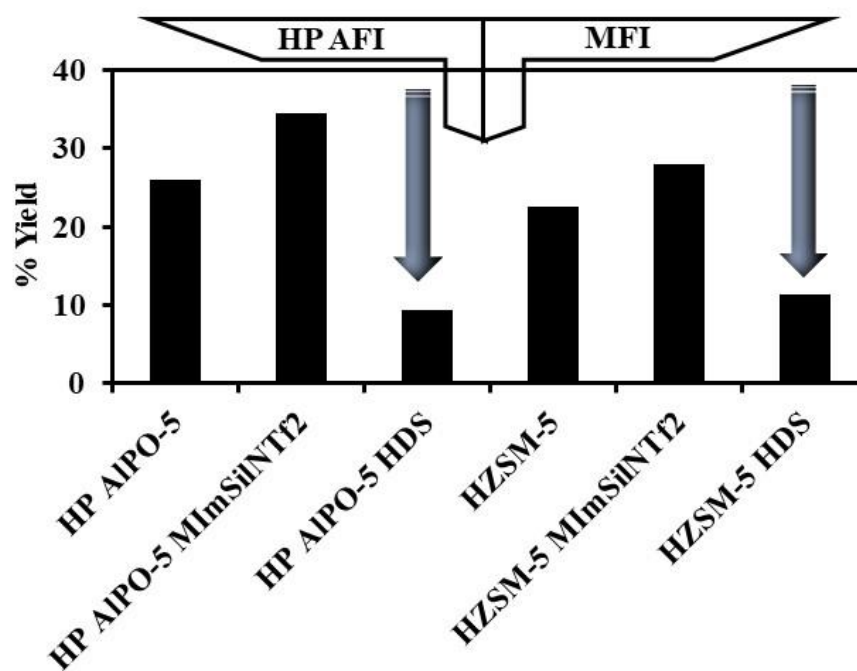


Figure 5. The percentage yield of caprolactam in the liquid-phase Beckmann rearrangement of cyclohexanone oxime using organosilane-(HDS) modified supports, compared to the bare support and its MImSiINTf₂ IL-MO hybrid. Reaction conditions: cyclohexanone oxime (0.1 g), chlorobenzene (0.1 g, internal standard), molar ratio of ionic liquid to oxime 0.05:1, benzonitrile (20 mL, solvent), at 130 °C for 6 hours.

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3 The influence of reaction temperature on the catalytic activity of the IL-MO hybrids was also
4 explored. For these studies, we investigated the catalytic activity of two sets of the supports and
5 hybrids: H-ZSM-5, H-ZSM-5 MImSilNTf₂, HP AlPO-5 and HP AlPO-5 MImSilNTf₂, at 150 and
6 170 °C. The full results, including % conversion of cyclohexanone oxime, % selectivity to CL,
7 and % yield of CL are given in Table S2, and the % yield of CL under the different conditions is
8 summarized in Figure 6. It was found that, as the reaction temperature was increased, there was a
9 progressive enhancement in oxime conversion and CL yield, with HP AlPO-5 MImSilNTf₂
10 achieving ~ 95 % conversion at 170 °C. Similarly, the HZSM-5 MImSilNTf₂ catalyst exhibited
11 superior performance at higher temperatures, when compared with its parent analogue. These
12 observations imply that the grafted IL remains stable at these higher temperatures (in line with our
13 characterization) allowing further optimization of reaction conditions to maximize CL yield.
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28 Zeolites and aluminophosphates have been predominantly employed as catalysts in vapor-phase
29 Beckmann rearrangement due to their inherent acidity^{29-38, 42, 43} A large proportion of these
30 catalysts tend to be less active and selective under milder, liquid-phase conditions, affording lower
31 yields of caprolactam. For example, Erigoni *et al.*²⁵ achieved caprolactam yield of 16 % using
32 microporous HZSM-5 (MFI) as the catalyst and 42 % using hierarchically porous HP ZSM-5 under
33 liquid-phase conditions. Hence, the 58 % yield achieved using HZSM-5 MImSilNTf₂, and the 71
34 % yield obtained with HP AlPO-5 MImSilNTf₂, which is reported in this work, represents a
35 marked improvement in catalytic performance for these systems under liquid-phase conditions.
36 To the best of our knowledge, improvements in caprolactam yield through appropriate
37 modification of zeolites and zeotypes with ionic liquids, which lead to the creation of ionic-liquid
38 metal-oxide hybrids, is hitherto unreported.
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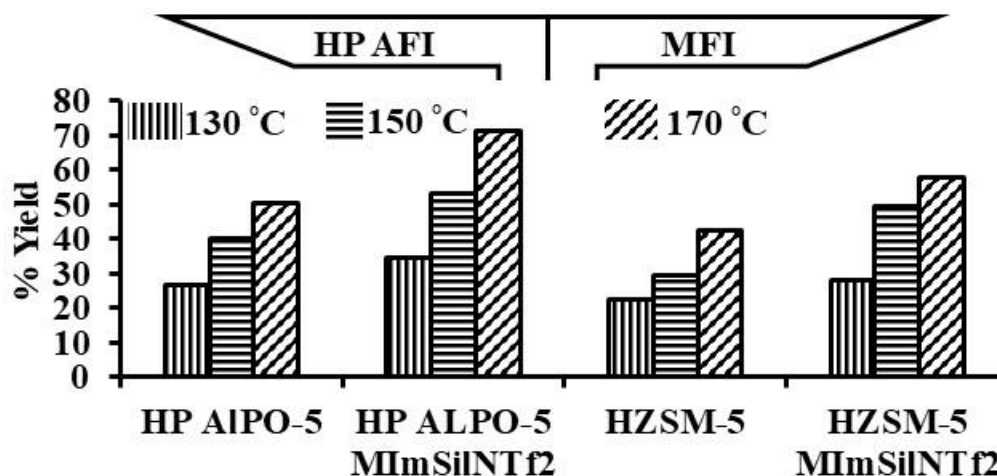


Figure 6. The effect of reaction temperature on the % yield of caprolactam in the liquid-phase Beckmann rearrangement of cyclohexanone oxime, using HP AlPO-5 and HZSM-5 supports, and their MImSilNTf₂ hybrids. Reaction conditions: cyclohexanone oxime (0.1 g), chlorobenzene (0.1 g, internal standard), molar ratio of ionic liquid to oxime 0.05:1, benzonitrile (20 mL, solvent), at 130 °C for 6 hours.

CONCLUSIONS

In summary, we have investigated the physicochemical and catalytic properties of ionic-liquid metal-oxide hybrids, in which ionic liquid-derived ions were covalently-anchored to the surface hydroxyl groups of the solid oxide. Our design strategy targeted the low-temperature, liquid-phase Beckmann rearrangement of cyclohexanone oxime to caprolactam, by modifying the hydrophobicity of the microporous and hierarchical catalysts through the anchored ionic liquid. Differences in the catalytic activity for liquid-phase BR highlighted the importance of the framework type, the nature of its porosity, and how a judicious choice of hydrophobic ionic liquids

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3 can improve caprolactam yield at low temperatures. The importance of the IL-MO hybrids in
4 modifying the surface and its influence in the reaction pathway was also probed using
5 complementary grafting procedures. It was also noteworthy that the IL-MO hybrids display
6 enhanced stability at higher reaction temperatures, which, combined with the benefits of using
7 hierarchical supports for efficient mass-transport, offers adequate scope for the industrial
8 application of these materials in other liquid-phase catalytic transformations.
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20 ASSOCIATED CONTENT

21 Supporting Information

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24 Supporting Information (SI) available: Synthesis procedure for AlPO-5, 1-methyl-3-
25 (propyltrimethoxysilane)imidazolium chloride (MImSilCl) and 1-methyl-3-
26 (propyltrimethoxysilane)imidazolium bistriflimide (MImSilNTf₂); C, H, N elemental analyses;
27 textural characterisation, including N₂ adsorption-desorption isotherms and pore size distributions
28 of catalytic materials, ²⁹Si and ¹³C MAS NMR characterisation; thermogravimetric analyses; FTIR
29 spectra of HP AlPO-5 and its IL-hybrids, and H ZSM-5 and its hybrids; ¹H NMR spectra for
30 MImSilCl and MImSilNTf₂; catalytic results; images of catalysts at the water-oil interface.
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19 **Notes**
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23 The authors declare no competing financial interest.
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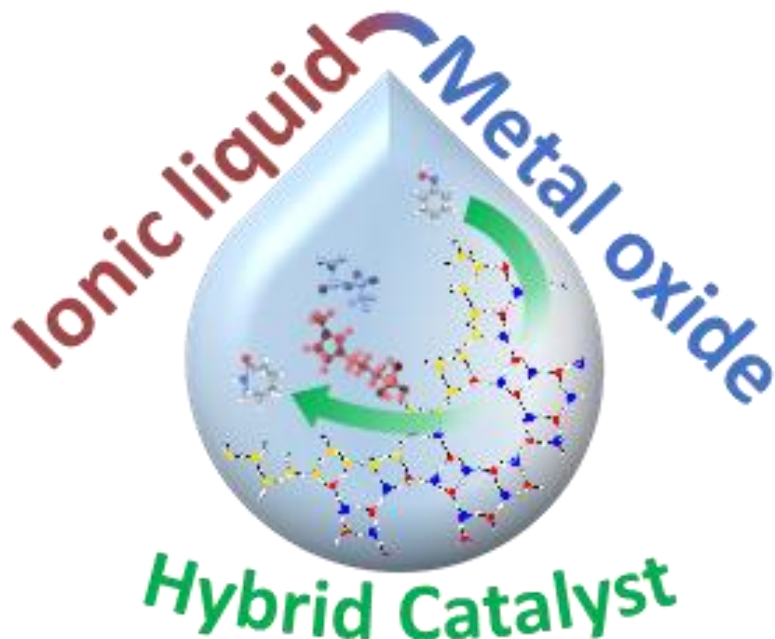
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GRAPHICAL ABSTRACT**SYNOPSIS**

Covalently-anchored ionic liquids modify the hydrophobicity of inorganic oxides to enhance their catalytic activity in the liquid-phase Beckmann rearrangement.