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

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ABSTRACT

We report the design of stable, ionic liquid-hybrids, covalently-anchored to the framework architectures of microporous and hierarchical solid supports. The ionic liquid moieties that are anchored to the framework facilitate enhanced mass-transport, and afford superior catalytic performance in the Beckmann rearrangement of cyclic oximes at low-temperatures. The ionic liquid-metal oxide (IL-MO) hybrids also play an important role in modifying the reaction

pathway and synergistic enhancements in catalytic properties are attributed to the increased hydrophobicity of the anchored, imidazolium-based ionic liquid.

KEYWORDS: Ionic liquid hybrids, Hydrophobic surface, Hierarchical oxides, Beckmann rearrangement, Caprolactam.

INTRODUCTION

The design of functional, inorganic–organic hybrid catalysts is emerging as an effective route to resolve some of the challenges facing process chemistry, including the sustainable production of bulk and fine chemicals.¹ The synergic effect of both inorganic and organic moieties in these hybrid materials leads to remarkable improvements in catalytic performance in many applications, including acid-base catalysis, chiral transformations, polymerization and selective oxidation. Catalytic reactions that have benefited from this approach include *trans*-esterification,² Knoevenagel condensation,³ Sonogashira coupling,⁴ the synthesis of cyclic carbonates from CO₂ and epoxide,⁵ asymmetric epoxidation,⁶ hydrogenation,⁷ ethylene polymerization,⁸ dehydration,⁹ and the selective oxidation of sulfides and alcohols.¹⁰ However, whilst catalytically efficient, the instability of many of these hybrid materials limits their widespread application.

More recently, hybrid materials created by incorporating ionic liquids (ILs) into solid-oxides have attracted increasing interest, owing to their relatively high boiling point, low vapor pressure, high thermal and chemical stability, and versatile functionality.¹¹ Different classes of ILs, including task-specific ILs (TSIL) and Brønsted-acidic ILs (BAIL), have been employed in catalysis, extraction, chemical analyses and other industrial applications.¹² For example, Visser

et al. reported a series of hydrophobic TSILs that can be used to extract toxic, heavy-metal cations from water. These TSILs, containing a urea-, thiourea-, or thioether-substituted alkyylimidazolium cation with the $[\text{PF}_6]^-$ anion, were found to selectively coordinate Hg^{2+} and Cd^{2+} ions.¹³ Hybrid materials of ILs, including poly(ionic liquid)s (PILs) and IL-silica gels (sometimes referred to as ionogels), have found extensive application as catalysts for many organic transformations.^{14, 15} Recently, we reported the preparation of a stable IL gel (a hybrid of silica and a functionalized acidic IL, triethylammonium propanesulfonate bistriflimide) that exhibits superior catalytic performance in the dehydration of *rac*-1-phenyl ethanol.¹⁶

Supported ionic liquid phases (SILPs), in which a thin layer of IL is deposited on to a supporting matrix, have also emerged as promising candidates in the last few years and are of considerable interest as functional catalysts and adsorbents.^{17,18} However, the stability of SILPs is a concern, as leaching of the ionic liquid moiety from the inorganic oxide surface can impact their recyclability, particularly in liquid phase reactions.¹⁹ To address the issue of leaching, covalent anchoring has been used to chemically attach ILs to a matrix - for example *via* bonds to surface hydroxyl groups on a metal-oxide support.²⁰ Additionally, to overcome the diffusion limitations of microporous supports employed, such as zeolites and aluminophosphates, hierarchically-porous (HP) zeolite and oxide analogues have been developed.²¹⁻²³ These HP materials are characterized by having multiple levels of porosity (including micro- (< 2 nm), meso- (2-50 nm) and/or macro- (> 50 nm) pores). Micro-meso zeolites, for example, can advantageously combine the catalytic features of the microporous parent framework with the improved access and transport properties associated with the mesoporous network.²⁴ Therefore, as well as overcoming diffusion limitations, HP materials broaden substrate scope by accommodating larger reactants, expanding the range of catalytic applications.²⁵

Given our interest in developing sustainable methodologies using a green chemistry approach, we have investigated the conventional homogeneous process to produce cyclic lactams, which are important feedstocks in the polymer industry. The Beckmann rearrangement (BR) of cyclic oximes to their corresponding lactam, is conventionally achieved using a mineral acid catalyst (typically sulfuric acid or oleum).²⁶ However, the use of such mineral acid catalysts necessitates a neutralization step that is detrimental to the atom efficiency of the process. As such, there has been considerable interest in designing heterogeneous catalysts for the industrial BR,^{27,28} as reflected in the diversity of research publications and patents describing solid-acid catalysts (including zeolites,²⁹⁻³³ metal-modified zeolites,³⁴⁻³⁸ mesoporous silica,³⁹⁻⁴¹, SAPOs,^{38,42,43} metal oxides or supported metal oxides⁴⁴⁻⁵¹ that operate under vapor-phase conditions ($\geq 300\text{ }^{\circ}\text{C}$). However, many of these solid-acid BR catalysts have low selectivity towards the desired lactam product and experience relatively fast deactivation due to the high temperatures employed.⁵² The presence of active sites such as terminal silanol groups and strong Brønsted acidic sites has been identified as detrimental to catalytic performance using these solid catalysts.^{48,49,52} Many researchers have attempted to incorporate suitable modifiers or diluents to the heterogeneous BR catalysts and/or processes to mitigate, or limit, the role of stronger acid sites. One such modification was the continuous addition of methanol,²⁷ which caps terminal silanol sites with the methoxy moiety. Whilst effective, the use of methanol necessitates additional processing steps, leading to increased costs and reduced efficiency. Furthermore, even though a continuous catalytic process is advantageous in many aspects, coking and fast deactivation of solid catalysts, rigorous reaction conditions, and a high energy input, warrants research into more sustainable liquid-phase conditions.⁵³⁻⁵⁶ Hence it is desirable to design efficient, solid-acid catalysts that can

operate under the conditions of the liquid-phase BR (LBR), to mitigate the formation of condensation by-products.^{56,57}

The advantages of ILs in the liquid-phase Beckmann rearrangement (LBR), either as the reaction medium, or as additives to improve the water tolerance of Lewis acids, is known.⁵⁸⁻⁶⁰ For example, the hydrophobicity and water-immiscibility of a TSIL comprising the ethylimidazolium cation with sulfonyl chloride, and PF_6^- as anion, has been exploited in the water-assisted extraction of caprolactam (CL) from the BR reaction mixture.⁶¹ Moreover, when metaboric acid was used as a catalyst in an IL reaction medium,⁶² the acidity of metaboric acid, combined with the hydrophobic nature of the IL, was found to achieve better conversion of oximes in the LBR.

When Karimi *et al.* confined the relatively hydrophobic IL, 1-methyl-3-octylimidazolium hydrogen sulfate ($[\text{MOcIm}]\text{HSO}_4$), inside the meso-channels of SBA-15-functionalized propylsulfonic acid, the SBA-15 hybrid exhibited higher catalytic performance than the bare support in esterification reactions.⁶³ The superior activity was explained on the basis of the hydrophobic nature of the *n*-octyl substituent of the IL, which, by repelling water from the catalyst surface and inhibiting the diffusion of water into the pores, improved the accessibility of the active sites for organic substrates.

Herein, we present an interesting synergism of IL ions supported on microporous and hierarchical architectures, for the LBR of cyclohexanone oxime (Scheme 1) inspired by the attenuating affect achieved by co-feeding methanol into the fluidized bed reactor of the commercial MFI catalyst.²⁷ It was proposed that the methanol reacts selectively with the terminal silanols of the zeolite to form methoxy groups, thereby minimizing side reactions. The zeolite powder in the fluidized bed reactor is continuously regenerated and methanol is recycled during

this process. Thus, we proposed that, by covalent anchoring of stable ions derived from an IL, we could achieve permanent capping of unwanted hydroxyls present in the catalysts. By immobilizing the IL *via* alkoxy silane groups to surface hydroxyl groups of the support material, it has been possible to create stable, composite catalysts with enhanced hydrophobicity around the active site. The result is a robust IL-MO hybrid exhibiting improved yield of CL in the LBR.

Scheme 1. The structure of the ionic liquids MImSiCl (A) and MImSiINTf₂ (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, followed by triethylamine (7.4 mL, Sigma Aldrich), also dropwise. Distilled water (40 mL) was added, and the resulting white slurry stirred for 1 hour. The gel was transferred to a Teflon-lined, stainless-steel autoclave and crystallized under hydrothermal conditions in a heated fan-assisted oven (WF-30 Lenton) at 200 °C for 24 hours. The solid product was collected *via* vacuum filtration and washed with deionized water (500 mL). The product was dried overnight in an oven at 80 °C. The as-synthesized catalyst was calcined in a tube furnace under a flow of air at 600 °C (3 °C min⁻¹ ramp rate) for 16 hours, yielding a white powder of HP AlPO-5.

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

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

Procedure for grafting IL on to support oxide: The covalent anchoring of ionic liquid to the support materials was achieved following the reported protocol.⁶⁴ The dried support (1 g) was transferred to a RBF containing dry toluene (50 mL, Sigma Aldrich). The IL (0.5 mmol) was added to the RBF, which was refluxed for 20 hours under constant stirring. The reaction mixture was cooled to room temperature, and the solid collected by vacuum filtration. Unreacted IL was removed by soxhlet extraction with dichloromethane solvent. The resulting IL-MO hybrid materials were first dried in low vacuum, and then at 90 °C with high vacuum on a Schleck line.

Procedure for the liquid phase Beckman rearrangement: Cyclohexanone oxime (0.1 g, Sigma Aldrich), molar ratio of ionic liquid to oxime 0.05:1, anhydrous benzonitrile (20 mL, Sigma Aldrich), and the internal standard, anhydrous chlorobenzene (0.1 g, Sigma Aldrich) were added to a three-necked RBF fitted with a reflux condenser, stopper, and rubber septum. Under constant nitrogen atmosphere, the reaction was heated to 130 °C under stirring. The reaction was monitored by sampling on an hourly basis, and analyzed by gas chromatography using a Perkin Elmer GC Clarus 480 with capillary column and flame-ionization detector (FID). Reagents and products were quantified against the internal standard, chlorobenzene.

RESULTS AND DISCUSSION

In the following discussion, microporous and hierarchically-porous (HP) analogues of the aluminosilicate, H-ZSM-5 (MFI), and the aluminophosphate, AlPO-5 (AFI), are used as support materials. Herein, these frameworks are designated AlPO-5, HP AlPO-5, H-ZSM-5, and HP ZSM-5. Whilst a soft, dual-templating (bottom-up) approach was used to introduce hierarchical porosity into AlPO-5, the hierarchical H-ZSM-5 was formed by post-synthetic desilication (a top-down approach).^{23,25} One of two imidazolium ILs, 1-methyl-3-

(propyltrimethoxysilane)imidazolium chloride (MImSiCl) or 1-methyl-3-(propyltrimethoxysilane)-imidazolium bistriflimide (MImSiNTf₂), was covalently anchored to the framework *via* the alkoxy silane group.

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

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

by C, H and N elemental analysis (Table S1), which shows these elements to be present in quantities that correlate with the amount 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 $\sim 350^\circ\text{C}$, 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 $\sim 230^\circ\text{C}$ and another after 430°C , whereas the MImSiNTf₂-based hybrids possess a single, distinct weight loss $> 350^\circ\text{C}$. 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 of the hydroxyl groups present inside the pore structure (i.e. defect silanols or nest silanols) are responsible for the activation of oxime molecules, while the terminal silanols are responsible for hydrolysis of oxime to the ketone by-product.^{27,56} In contrast, the catalytic activity of HP AlPO-5 is derived mainly from the pendant silanol groups present in the mesopores (originating from the surfactant template), with some contribution from Al-OH and P-OH defect sites.²³

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

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

rearrangement, but also enhances catalyst selectivity by excluding the water by-product that is generated during the reaction.

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.

In contrast to HZSM-5, HP ZSM-5 materials were found to operate best without modification. In line with earlier observations, the hydrophobic MImSiINTf₂ variant in HZMS-5 and HPZSM-5 affords superior catalytic performance when compared with the hydrophilic MImSiCl analogue. More importantly, the catalytic activity of HP ZSM-5 is influenced primarily by the accessible acid sites and hierarchical porosity; and the hydrophilic/hydrophobic properties of the IL are not the principal determinant, when compared with the HP AlPO-5 framework. Hence, further surface modification studies using organosilane were undertaken in order to probe the effect of hydrophobicity on the HZSM-5 and HP AlPO-5 supports.

The enhanced hydrophobicity of HP AlPO-5 MImSiINTf₂ is evidenced by the contact angle and the shape of the water drops on the surface of this hybrid. Whilst water forms a spherical droplet on the surface of the HP AlPO-5 MImSiINTf₂ hybrid wafer (contact angle 58.4 °), it adheres to the surface of the chloride counterpart (contact angle ~ 0 °), and also the bare oxide (Figure 4). In addition, when IL-MO powders were combined with a water/*n*-hexane mixture, the more hydrophobic HP AlPO-5 MImSIINTf₂ was found to interact with the oil layer, whereas the parent framework and the chloride-IL hybrid counterpart preferentially interacted with the water layer (Figure S8).

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

MImSiNTf₂ 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.

The influence of reaction temperature on the catalytic activity of the IL-MO hybrids was also explored. For these studies, we investigated the catalytic activity of two sets of the supports and hybrids: H-ZSM-5, H-ZSM-5 MImSiINTf₂, HP AlPO-5 and HP AlPO-5 MImSiINTf₂, at 150 and 170 °C. The full results, including % conversion of cyclohexanone oxime, % selectivity to CL, and % yield of CL are given in Table S2, and the % yield of CL under the different conditions is summarized in Figure 6. It was found that, as the reaction temperature was increased, there was a progressive enhancement in oxime conversion and CL yield, with HP AlPO-5 MImSiINTf₂ achieving ~ 95 % conversion at 170 °C. Similarly, the HZSM-5 MImSiINTf₂ catalyst exhibited superior performance at higher temperatures, when compared with its parent analogue. These observations imply that the grafted IL remains stable at these higher temperatures (in line with our characterization) allowing further optimization of reaction conditions to maximize CL yield.

Zeolites and aluminophosphates have been predominantly employed as catalysts in vapor-phase Beckmann rearrangement due to their inherent acidity^{29-38, 42, 43}. A large proportion of these catalysts tend to be less active and selective under milder, liquid-phase conditions, affording lower yields of caprolactam. For example, Erigoni *et al.*²⁵ achieved caprolactam yield of 16 % using microporous HZSM-5 (MFI) as the catalyst and 42 % using hierarchically porous HP ZSM-5 under liquid-phase conditions. Hence, the 58 % yield achieved using HZSM-5 MImSiINTf₂, and the 71 % yield obtained with HP AlPO-5 MImSiINTf₂, which is reported in this work, represents a marked improvement in catalytic performance for these systems under liquid-phase conditions. To the best of our knowledge, improvements in caprolactam yield through appropriate modification of zeolites and zeotypes with ionic liquids, which lead to the creation of ionic-liquid metal-oxide hybrids, is hitherto unreported.

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 MImSiINTf₂ 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 can improve caprolactam yield at low temperatures. The importance of the IL-MO hybrids in modifying the surface and its influence in the reaction pathway was also probed using complementary grafting procedures. It was also noteworthy that the IL-MO hybrids display enhanced stability at higher reaction temperatures, which, combined with the benefits of using hierarchical supports for efficient mass-transport, offers adequate scope for the industrial application of these materials in other liquid-phase catalytic transformations.

ASSOCIATED CONTENT

Supporting Information

Supporting Information (SI) available: Synthesis procedure for AlPO-5, 1-methyl-3-(propyltrimethoxysilane)imidazolium chloride (MImSilCl) and 1-methyl-3-(propyltrimethoxysilane)imidazolium bistriflimide (MImSilNTf₂); C, H, N elemental analyses; textural characterisation, including N₂ adsorption-desorption isotherms and pore size distributions of catalytic materials, ²⁹Si and ¹³C MAS NMR characterisation; thermogravimetric analyses; FTIR spectra of HP AlPO-5 and its IL-hybrids, and H ZSM-5 and its hybrids; ¹H NMR spectra for MImSilCl and MImSilNTf₂; catalytic results; images of catalysts at the water-oil interface.

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REFERENCES

1. Wight, A. P.; Davis, M. E. Design and Preparation of Organic–Inorganic Hybrid Catalysts. *Chem. Rev.* **2002**, *102*, 3589-3614. DOI: 10.1021/cr010334m
2. Cruz, F. T.; Cardoso, D. Catalytic transesterification using a silica hybrid containing encapsulated polyacrylates. *Appl. Catal. A: Gen.* **2017**, *548*, 83-88. DOI: 10.1016/j.apcata.2017.09.003
3. Brooks, A. C.; France, L.; Gayot, J.; Pui, L. C.; Li, J. H.; Sault, Stafford, R. A.; Wallis, J. D.; Stockenhuber, M. A designed organic–zeolite hybrid acid–base catalyst. *J. Catal.* **2012**, *285*, 10-18. DOI: 10.1016/j.jcat.2011.09.004
4. Borja, G.; Monge-Marcet, A.; Pleixats, R.; Parella, T.; Cattoën, X.; Chi Man, M. W. Recyclable Hybrid Silica-Based Catalysts Derived from Pd–NHC Complexes for Suzuki, Heck and Sonogashira Reactions. *Eur. J. Org. Chem.* **2012**, *19*, 3625-3635. DOI: 10.1002/ejoc.201200205
5. Srivastava, R.; Srinivas, D.; Ratnasamy, P. Zeolite-based organic–inorganic hybrid catalysts for phosgene-free and solvent-free synthesis of cyclic carbonates and carbamates at mild conditions utilizing CO₂. *Appl. Catal. A: Gen.* **2005**, *289*, 128-134. DOI: 10.1016/j.apcata.2005.04.055
6. Huang, J.; Fu, X.; Miao, Q. Catalytic asymmetric epoxidation of unfunctionalized olefins using a series novel type of layered crystalline organic polymer–inorganic hybrid zinc phosphonate–phosphate immobilized aryldiamine modified chiral salen Mn(III) complex. *Appl. Catal. A: Gen.* **2011**, *407*, 163-172. DOI: 10.1016/j.apcata.2011.08.035

7. Antonettia, C.; Toniolob, L.; Forted, G. C.; Ghignolia, C.; Ishake, R.; Cavanif, F.; Galletti, A. M. R. A hybrid polyketone–SiO₂ support for palladium catalysts and their applications in cinnamaldehyde hydrogenation and in 1-phenylethanol oxidation. *Appl. Catal. A: Gen.* **2015**, *496*, 40-50. DOI: 10.1016/j.apcata.2015.01.045
8. Barrera, E. G.; Stedile, F. C.; de Souza, M. O.; Miranda, M. S. L.; de Souza, R. F.; Gusmao, K. B. Ethylene polymerization using metallocene catalyst supported on hybrid indenyl silica produced by sol–gel process. *Appl. Catal. A: Gen.* **2013**, *462- 463*, 1-7. DOI: 10.1016/j.apcata.2013.04.021
9. Ivanova, S.; Nitsch, X.; Romero-Sarria F. New class of acid catalysts for methanol dehydration. *Stud. Surf. Sci. Catal.* **2010**, *175*, 601-604. DOI: 10.1016/S0167-2991(10)75117-X
10. Li, J.; Huang, X.; Yang, S.; Xu Y.; Hu, C. Controllable Synthesis, Characterization, and Catalytic Properties of Three Inorganic–Organic Hybrid Copper Vanadates in the Highly Selective Oxidation of Sulfides and Alcohols. *Cryst. Growth Des.* **2015**, *15*, 1907-1914. DOI: 10.1021/acs.cgd.5b00086
11. Handy S. T. *Ionic liquids-Classes and properties*; InTech, Croatia, 2011.
12. Giernoth, R. Task-Specific Ionic Liquids. *Angew. Chem. Int. Ed.*, **2010**, *49*, 2834-2839. DOI: 10.1002/anie.200905981
13. Visser, A.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis Jr, J. H.; Rogers, R. D. Task-Specific Ionic Liquids Incorporating Novel Cations for the Coordination and Extraction of Hg²⁺ and Cd²⁺: Synthesis, Characterization, and

- Extraction Studies. *Environ. Sci. Technol.*, **2002**, *36*, 2523-2529. DOI: 10.1021/es0158004
14. Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071-2083. DOI: 10.1021/cr980032t
15. Marr, P. C.; Marr, A. C. Ionic liquid gel materials: applications in green and sustainable chemistry. *Green Chem.* **2016**, *18*, 105-128. DOI: 10.1039/C5GC02277K
16. Wang, Y. -M.; Ulrich, V.; Donnelly, G. F.; Lorenzini, F.; Marr A. C.; Marr, P. C. A Recyclable Acidic Ionic Liquid Gel Catalyst for Dehydration: Comparison with an Analogous SILP Catalyst. *ACS Sustainable Chem. Eng.* **2015**, *3*(5), 792-796. DOI: 10.1021/sc5008303
17. Fehrmann, R., Rissager, A., Haumann, M., Eds. Supported Ionic Liquids - Fundamentals and Applications, Wiley-VCH: Weinheim, 2013.
18. Haumann, M.; et al. Catalysis in Ionic Liquids: From Catalyst Synthesis to Application. In *RSC Catalysis Series No. 15*; Hardacre, C., Parvulescu, V., Eds. RSC Publishing: Cambridge, U.K., 2014.
19. Liévano, J. F. P.; Díaz, L. A. C. Synthesis and Characterization of 1-Methyl-3-Methoxysilyl Propyl Imidazolium Chloride – Mesoporous Silica Composite as Adsorbent for Dehydration in Industrial Processes. *Mat. Res.* **2016**, *19*(3), 534-540. DOI: 10.1590/1980-5373-MR-2015-0561
20. Xin, B.; Hao, J. Imidazolium-based ionic liquids grafted on solid surfaces. *Chem. Soc. Rev.* **2014**, *43*, 7171-7187. DOI: 10.1039/C4CS00172A

21. Palkovits, R.; Schmidt, W.; Ilhan, Y.; Erdem-Senatalar, A.; Schüth, F. Crosslinked TS-1 as stable catalyst for the Beckmann rearrangement of cyclohexanone oxime. *Micro. Meso. Mater.* **2009**, *117*, 228-232. DOI: 10.1016/j.micromeso.2008.06.041
22. Kim, J.; Park, W.; Ryoo, R. Surfactant-Directed Zeolite Nanosheets: A High-Performance Catalyst for Gas-Phase Beckmann Rearrangement. *ACS Catal.* **2011**, *1*, 337-341. DOI: 10.1021/cs100160g
23. Newland, S. H.; Sinkler, W.; Mezza, T.; Bare, S. R.; Carravetta, M.; Haies, I. M.; Levy, A.; Keenan, S.; Raja, R. Expanding Beyond the Micropore: Active-Site Engineering in Hierarchical Architectures for Beckmann Rearrangement. *ACS Catal.* **2015**, *5*, 6587-6593. DOI: 10.1021/acscatal.5b01595
24. Vargas, M. C.; Garcia, A.; Ochoa-Hernandez, C.; Cejka, J.; Garcia Munoz, R. A.; Serrano, D. P. Effect of hierarchical porosity in Beta zeolites on the Beckmann rearrangement of oximes. *Catal. Sci. Technol.* **2017**, *7*, 181-190. DOI: 10.1039/C6CY01895E
25. Erigoni, A.; Newland, S. H.; Paul, G.; Marchese, L.; Raja, R.; Gianotti, E. Creating Accessible Active Sites in Hierarchical MFI Zeolites for Low-Temperature Acid Catalysis. *ChemCatChem.* **2016**, *8*, 3161-3169. DOI: 10.1002/cctc.201600729
26. Weissmehl, K., Arpe, H. R. Eds. Industrial Organic Chemistry, 3rd ed.; Wiley: Weinheim, 1997.

27. Izumi, Y.; Ichihashi, H.; Shimazu, Y.; Kitamura, M.; Sato, H. Development and Industrialization of the Vapor-Phase Beckmann Rearrangement Process. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1280-1287. DOI: 10.1246/bcsj.80.1280
28. Chu, Y.; Ji, P.; Yi, X.; Li, S.; Wu, P.; Zheng, A.; Deng, F. Strong or weak acid, which is more efficient for Beckmann rearrangement reaction over solid acid catalysts?. *Catal. Sci. Technol.* **2015**, *5*, 3675-3681. DOI: 10.1039/C5CY00619H
29. Landis, P. S.; Venuto, P. B. Organic reactions catalyzed by crystalline aluminosilicates: IV. Beckmann rearrangement of ketoximes to amides. *J. Catal.* **1966**, *6*, 245-252. DOI: 10.1016/0021-9517(66)90055-8
30. Thangaraj, A.; Sivasanker S.; Ratnasamy, P. Catalytic properties of titanium silicalites: IV. Vapour phase Beckmann rearrangement of cyclohexanone oxime. *J. Catal.* **1992**, *137*, 252-256. DOI: 10.1016/0021-9517(92)90154-A
31. Heitmann, G. P.; Dahlhoff, G. J.; Niederer, P. M.; Holderich, W. F. Active Sites of a [B]-ZSM-5 Zeolite Catalyst for the Beckmann Rearrangement of Cyclohexanone Oxime to Caprolactam. *J. Catal.* **2000**, *194*, 122-129. DOI: 10.1006/jcat.2000.2928
32. Komatsu, T.; Maeda, T.; Yashima, T. *Micro. Meso. Mater.* Kinetic study on the effect of solvent in 'vapor-phase' Beckmann rearrangement of cyclohexanone oxime on silicalite-1. **2000**, *35-36*, 173-180. DOI: 10.1016/S1387-1811(99)00218-8
33. Dai, L.; Koyama, K.; Miyamoto, M.; Tatsuni, T. Highly selective vapor phase Beckmann rearrangement over H-USY zeolites. *Appl. Catal. A: Gen.* **1999**, *189*, 237-242. DOI: 10.1016/S0926-860X(99)00280-X

34. Roseler, J.; Heitmann, G. Holderich, W. F. *Appl. Catal. A: Gen.* Vapor-phase Beckmann rearrangement using B-MFI zeolites. **1996**, *144*, 319-333. DOI: 10.1016/0926-860X(96)00127-5
35. Holderich, W. F., Roseler, J.; Heitmann, G. Liebens, A. T. The use of zeolites in the synthesis of fine and intermediate chemicals. *Catal. Today*. **1997**, *37*, 353-366. DOI: 10.1016/S0920-5861(97)81094-2
36. Ngamcharussrivichai, C.; Wu, P.; Tatsumi, T. Liquid-phase Beckmann rearrangement of cyclohexanone oxime over mesoporous molecular sieve catalysts, *J. Catal.* **2004**, *227*, 448–458. DOI: 10.1016/j.jcat.2004.08.008
37. Murthy, K. V. V. S. B. S. R.; Chandrakala, M.; Kulkarni, S. J.; Raghavan, K. V. Beckmann rearrangement of cyclohexanone oxime over modified molecular sieves. *Indian J. Chem. Tech.* **2001**, *8*, 368-370.
38. Thomas, B.; Sugunan, S. Rare-earth (Ce^{3+} , La^{3+} , Sm^{3+} , and Re^{3+}) exchanged Na-Y zeolites and K-10 clay as solid acid catalysts for the synthesis of benzoxazole via Beckmann rearrangement of salicylaldoxime. *Micro. Meso. Mater.* **2006**, *96*, 55-64. DOI: doi.org/10.1016/j.micromeso.2006.06.005
39. Li, W.; Lu, A.; Palkovits, R.; Schmidt, W.; Spliethoff, B.; Schuth, F. Hierarchically Structured Monolithic Silicalite-1 Consisting of Crystallized Nanoparticles and Its Performance in the Beckmann Rearrangement of Cyclohexanone Oxime. *J. Am. Chem. Soc.* **2005**, *127*, 12595-12600. DOI: 10.1021/ja052693v

40. Palkovits, R.; Ilhan, Y.; Schmidh, W.; Yang, C. M.; Erdam-Sentalar, A.; Schuth, F. *Stud. Surf. Sci. and Catal.* Beckmann rearrangement on microporous and mesoporous silica. **2005**, *158*, 1255-1262. DOI: 10.1016/S0167-2991(05)80472-0
41. Ko, A.; Hung, C.; Chen C.; Ouyang, K. Mesoporous molecular sieve Al-MCM-41 as a novel catalyst for vapor-phase Beckmann rearrangement of cyclohexanone oxime. *Catal. Lett.* **2001**, *71*, 219-224. DOI: 10.1023/A:1009038701442
42. Singh, P.; Bandyopadhyay, S. R.; Hegdey, S. G.; Rao, B. S. Vapor phase beckmann rearrangement of cyclohexanone oxime over SAPO-11 molecular sieve. *Appl. Catal. A: Gen.* **1996**, *136*, 249-263. DOI: 10.1016/0926-860X(95)00303-7
43. Gianotti, E.; Manzoli, M. Potter, M. E.; Shetti, V. N.; Sun, D.; Paterson, J.; Mezza, T. M.; Levy, A.; Raja, R. Rationalising the role of solid-acid sites in the design of versatile single-site heterogeneous catalysts for targeted acid-catalysed transformations. *Chem. Sci.* **2014**, *5*, 1810-1819. DOI: 10.1039/C3SC53088D
44. Conesa, T. D.; Mokaya, R.; Yang, Z.; Luque, R.; Campelo, J. M.; Romero, A. A. Novel mesoporous silicoaluminophosphates as highly active and selective materials in the beckmann rearrangement of cyclohexanone and cyclododecanone oximes. *J. Catal.* **2007**, *252*, 1-10. DOI: 10.1016/j.jcat.2007.09.006
45. Sato, S.; Urabe, K.; Izumi, Y. *J. Catal.* Vapor-phase Beckmann rearrangement over silica-supported boron catalyst prepared by vapor decomposition method. **1986**, *102*, 99-108. DOI: 10.1016/0021-9517(86)90144-2

46. Curtin, T.; McMonagle, J. B.; Hodnett, B. K.; Influence of boria loading on the acidity of B_2O_3/Al_2O_3 catalysts for the conversion of cyclohexanone oxime to caprolactam. Appl. Catal. A: Gen., **1992**, 93, 91-101. DOI: 10.1016/0926-860X(92)80296-O
47. Ushikubo, T.; Wada, K. Vapor-Phase Beckmann Rearrangement over Silica-Supported Tantalum Oxide Catalysts. *J. Catal.* **1994**, 148, 138-148. DOI: 10.1006/jcat.1994.1195
48. Kob, N.; Drago, R. S. Catalysis of the formation of ϵ -caprolactam from cyclohexanone oxime by tungsten oxide solid acids. *Catal. Lett.* **1997**, 49, 229-234. DOI: 10.1023/A:1019017624389
49. Ichihashi, H.; Ishida, M.; Shiga, A.; Kitamura, M.; Suzuki, T.; Suenobu, K.; Sugita, K. The catalysis of vapor-phase Beckmann rearrangement for the production of ϵ -caprolactam. *Catal. Surv. Asia*, **2003**, 7, 261-270. DOI: 10.1023/B:CATS.0000008165.80991.05
50. Anilkumar, M.; Hoelderich, W. F. Gas phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam over mesoporous, microporous and amorphous Nb_2O_5 /silica catalysts: A comparative study. *Catal. Today*, **2012**, 198, 289-299. DOI: 10.1016/j.cattod.2012.01.043
51. Kumar, R.; Ponnada, S.; Enjamuri, N.; Pandey, J. K.; Chowdhury, B. Synthesis, characterization and correlation with the catalytic activity of efficient mesoporous niobia and mesoporous niobia–zirconia mixed oxide catalyst system. *Catal. Comm.* **2016**, 77, 42-46. DOI: 10.1016/j.catcom.2016.01.012

52. Aucejo, M. C. Burguet, A. Corma and V. Fornes. Beckman rearrangement of cyclohexanone-oxime on HNaY zeolites: kinetic and spectroscopic studies. *Appl. Catal. A: Gen.*, **1986**, 22, 187-200. DOI: 10.1016/S0166-9834(00)82628-7

53. Alzeer, M. I. M.; MacKenzie, K. J. D.; Keyzers, R. A. Porous aluminosilicate inorganic polymers (geopolymers): A new class of environmentally benign heterogeneous solid acid catalysts. *Appl. Catal. A: Gen.* **2016**, 524, 173-181. DOI: 10.1016/j.apcata.2016.06.024

54. Takahashi, T.; Kai T.; Nakao, E. Catalyst deactivation in the Beckmann rearrangement of cyclohexanone oxime over H-ZSM-5 zeolite and silica-alumina catalysts. *Appl. Catal. A: Gen.* **2004**, 262, 137-142. DOI: 10.1016/j.apcata.2003.11.040

55. Mao, D.; Lu, G.; Chen, Q.; Xie, Z. Zhang, Y. Catalytic Performance of B₂O₃/TiO₂-ZrO₂ for Vapor-Phase Beckmann Rearrangement of Cyclohexanone Oxime: The Effect of Boria Loading. *Catal. Lett.* **2001**, 77, 119-124. DOI: 10.1023/A:1012787028360

56. Takahashi, T.; Nasution, M. N. A.; Kai, T. Effects of acid strength and micro pore size on caprolactam selectivity and catalyst deactivation in vapor phase Beckmann rearrangement over acid solid catalysts. *Appl. Catal. A: Gen.* **2001**, 210, 339-344. DOI: 10.1016/S0926-860X(00)00828-0

57. Cambor, M. A., Corma, A.; Garcia, H.; Semmer-Herledan, V.; Valencia, S. Active sites for the liquid- phase beckmann rearrangement of cyclohexanone, acetophenone and cyclododecanone oximes, catalyzed by beta zeolites. *J. Catal.* **1998**, 177, 267-272. DOI: 10.1006/jcat.1998.2110

58. Wang, H.; Jia, L.; Hu, R.; Gao, M.; Wang, Y. One-pot conversion of cyclohexanol to ϵ -caprolactam using a multifunctional Na₂WO₄-acidic ionic liquid catalytic system. *Chin. J. Catal.* **2017**, *38*, 58-64. DOI: 10.1016/S1872-2067(16)62563-9
59. Kore, R.; Srivastava, R. A simple, eco-friendly, and recyclable bi-functional acidic ionic liquid catalysts for Beckmann rearrangement. *J. Mol. Catal. A: Chem.* **2013**, *376*, 90-97. DOI: 10.1016/j.molcata.2013.04.021
60. Maia, A.; Albanese, D. C. M.; Landini, D. Cyanuric Chloride Catalyzed Beckmann Rearrangement of Ketoximes in Biodegradable Ionic Liquids. *Tetrahedron*, **2012**, *68*, 1947-1950. DOI: 10.1016/j.tet.2011.12.051
61. Mao-cheng, W.; Hai-feng, D.; Jun-gang, Da-peng, C. L.; Feng. Brønsted Acidic Ionic Liquids: Efficient and Recyclable Catalytic Systems for Beckmann Rearrangement. *J. Chem. Res. Chin. Uni.* **2011**, *27*(6), 973-976. Article ID: 1005-9040(2011)-06-973-04
62. Guo, S.; Deng, Y. Environmentally friendly Beckmann rearrangement of oximes catalyzed by metaboric acid in ionic liquids. *Catal. Comm.* **2005**, *6*, 225-228. DOI: 10.1016/j.catcom.2005.01.003
63. Karimi, B.; Vafaezadeh, M. SBA-15-functionalized sulfonic acid confined acidic ionic liquid: a powerful and water-tolerant catalyst for solvent-free esterifications. *Chem. Commun.* **2012**, *48*, 3327-3329. DOI: 10.1039/C2CC17702A
64. Sing, K.S.W. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Appl. Chem.* **1982**, *54*, 2201-2218. DOI: 10.1351/pac198254112201

65. Valkenberg, M. H.; deCastro, C.; Hölderich, W. F. Immobilisation of ionic liquids on solid supports. *Green Chem.* **2002**, *4*, 88-93. DOI: 10.1039/B107946H
66. Heinze, M. T. Zill, J. C.; Matysik, J.; Einicke, W. D.; Glaser, R.; Stark, A. Solid–ionic liquid interfaces: pore filling revisited. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24359-24372. DOI: 10.1039/C4CP02749C
67. Asefa, T.; MacLachlan, M.; Coombs, N.; Ozin, G. Periodic mesoporous organosilicas with organic groups inside the channel walls. *Nature* **1999**, *402*, 867-871. DOI: 10.1038/47229
68. Gianotti, E.; Diaz, U.; Verty A.; Corma, A. Designing bifunctional acid–base mesoporous hybrid catalysts for cascade reactions. *Catal. Sci. Technol.* **2013**, *3*, 2677-2688. DOI: 10.1039/C3CY00269A
69. Babucci, M.; Akçay, A.; Balci, V.; Uzun, A. Thermal Stability Limits of Imidazolium Ionic Liquids Immobilized on Metal-Oxides. *Langmuir*, **2015**, *31*, 9163-9176. DOI: 10.1021/acs.langmuir.5b02519
70. Pringle, J. M.; Golding, J.; Baranyai, K.; Forsyth, C. M.; Deacon, G. B.; Scott J. L.; MacFarlane, D. R. The effect of anion fluorination in ionic liquids—physical properties of a range of bis(methanesulfonyl)amide salts. *New J. Chem.* **2003**, *27*, 1504-1510. DOI: 10.1039/B304072K.
71. Xu, S.; Sheng, H.; Ye, T.; Hu, D.; Liao, S. Hydrophobic aluminosilicate zeolites as highly efficient catalysts for the dehydration of alcohols. *Catal. Comm.* **2016**, *78*, 75-79. DOI: 10.1016/j.catcom.2016.02.006

GRAPHICAL ABSTRACT

SYNOPSIS

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