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1. Introduction

Catalytic transformation of lignocellulosic biomass and related platform molecules into valuable chemicals and fuel products represents an efficient strategy to decrease the current dependence on exhaustible resources.^{1–4} As one of such promising C_6 sugar-derived platform molecules, 5-hydroxymethylfurfural (HMF) has received greatly interest in green chemistry and sustainable chemical industry.^{4–6} HMF exhibits enormous synthetic potential and high reactivity, which are provided by the presence of three functional centers, the aldehyde group, hydroxymethyl group and furan

School of Environment, Northeast Normal University, 2555 Jingyue Street,

Changchun 130117, P.R. China. E-mail: guoyh@nenu.edu.cn † Electronic supplementary information (ESI) available. See DOI: 10.1039/

Design of Brønsted acidic ionic liquid functionalized mesoporous organosilica nanospheres for efficient synthesis of ethyl levulinate and levulinic acid from 5-hydroxymethylfurfural[†]

Daiyu Song, Jingyu Liu, Chaoyue Zhang and Yihang Guo 吵*

Brønsted acidic ionic liguids (BAILs) have brought new vitality in catalytic transformation of biomass to fuels and chemicals, but practical applications of BAILs suffer from drawbacks of slow diffusion and difficulty in separation. Chemical immobilization of BAILs is an effective way to circumvent these problems. Here, we demonstrate a series of monodispersed mesoporous organosilica nanosphere-immobilized BAIL catalysts, $[C_3PrIm][OTf]-MONSs$ ($C_3 = PrSO_3H$, OTf = SO_3CF_3), by a quaternary ammonium surfactant micelledirected liquid-interface assembly strategy followed by successive chemical modifications, and the particle size (180-360 nm) and pore morphology (periodic centrally radialized and 3D interconnected mesopores) of the catalysts are well-adjusted by changing the cations and/or anions of the surfactants as well as the preparation conditions. As-prepared [C₃PrIm][OTf]-MONSs serve as nanoreactors to transform an important biomass-derived platform molecule, 5-hydroxymethylfurfural, in ethanol and water media to valuable chemicals, ethyl levulinate (EL) and levulinic acid (LA). By the combination of their superstrong Brønsted acidic nature, outstanding open mesoporous spherical nanostructures and excellent textural properties, the [C₃PrIm][OTf]-MONSs exhibit high ethanolysis and hydrolysis activity and selectivity. The particle size and pore morphology of the catalysts significantly influence the selectivity and thereby the yield of the products. The cetyltrimethylammonium tosylate-directed [C₃PrIm][OTf]-MONSs catalyst with the smallest particle size (210 nm) and a wormhole-like interconnected mesostructure shows the highest yield of EL (93.6%) and LA (72.8%) under the optimum reaction conditions. The catalyst also displays good reusability in ethanolysis reaction, originating from chemical bonding [C₃PrIm][OTf] within the hydrophobic silica framework.

> ring, in its structure.⁷ HMF can be converted to a variety of targeted high value-added chemicals, including highly promising new biofuel candidates and important platform compounds. Among these, Brønsted acid catalyzed ringopening reactions of HMF in ethanol and water media can produce ethyl levulinate (EL) and levulinic acid (LA) in an atom economic approach.8,9 EL has been found to be extensively applied in the perfume and flavor industries and as a blending agent for diesel fuel formulation,^{10,11} while LA is one of the most attractive and important intermediates for the synthesis of a broad range of chemicals (e.g., diphenolic acid and δ -aminolevulinic acid), fuel additives (e.g., alkyl levulinates and y-valerolactone) and liquid hydrocarbon fuels.¹²⁻¹⁹ Although liquid Brønsted acids (e.g., H₂SO₄ and p-toluenesulfonic acid) show high efficiency for the target reactions, they suffer from severe problems of corrosiveness to equipment, pollution to the environment and difficulty in separation and recovery.²⁰⁻²² As for generally applied solid

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acids (*e.g.*, sulfated zirconia, sulfonic acid functionalized silica/carbon, acidic resins and zeolites), they bear the drawbacks of poor accessibility of the acid sites for the substrates and irreversible deactivation by the formation of by-products, humins, due to the oligomerization and polymerization of HMF on their surface.^{8,23,24} Therefore, the crucial challenge for efficient and selective synthesis of EL and LA from HMF is to develop recoverable and environmentally-benign Brønsted acid catalysts.

Here, we develop a novel solid acid, Brønsted acidic ionic liquid functionalized mesoporous organosilica nanospheres $([C_3PrIm][OTf]-MONSs, C_3 = PrSO_3H, Im = imidazole, OTf =$ SO₃CF₃), for high yield synthesis of EL and LA from ethanolysis and hydrolysis of HMF. Ionic liquids (ILs) have attracted considerable attention due to their distinguishing properties such as nonvolatility, strong dissolution and structural designability, and they are preferable innovative green solvents in chemical reactions; moreover, functionalized ILs have exhibited outstanding catalytic performances, thus bringing new vitality in numerous biomass transformation-associated processes.²⁵⁻²⁹ In this context, Brønsted acidic ILs (BAILs) have emerged. For example, C_nMIm-based BAILs show excellent catalytic activity and selectivity in the synthesis of 100% bio-based poly(ethylene 2,5-furandicarboxylate) from the esterification of ethylene glycol with biomass-derived 2,5-furandicarboxylic acid;³⁰ sulfonic acid-functionalized ILs display high selectivity and reactivity in conversion of chitin to LA (ref. 27) or synthesis of furylmethane derivatives from the condensation of furan with furfural.³¹ However, the practical applications of BAILs remain a challenge because they show high solubility in most of solvents, and thus tedious separations of BAILs from the reaction media for recycling are needed; meanwhile, the catalytic reactions are limited by diffusion processes owing to the high viscosity and low diffusion coefficients of BAILs. Chemical immobilization of BAILs on suitable supports is an effective way to circumvent these problems; meanwhile, the cost of BAILs can be reduced owing to a significantly decreased dosage. For examples, BAIL-functionalized organosilica hollow nanospheres,³² polysiloxane networks³³ and dendritic fibrous nitrogen-doped carbon nanospheres³⁴ as well as imine-linked COF (covalent organic framework)-confined BAILs³⁵ have been reported to exhibit excellent catalytic activity and high reusability in biomass conversion-associated processes.

Among various catalyst supports, mesoporous inorgano/ organosilicas, prepared by sol-gel chemistry, are one of the best choices due to their facilely-controlled morphologies and well-defined mesoporosities and thus excellent textural properties, which endow silica supported ILs distinguishing catalytic performances in comparison to bulk ILs through facilitating mass transfer and increasing active site populations.^{36,37} Moreover, in comparison to traditional mesoporous silicas, mesoporous organosilicas with a flexible silica/carbon framework and high hydrothermal stability as well as a tunable morphology and surface hydrophilicity/

better support candidates hydrophobicity are in nanocatalysis.³⁸ In the current work, we design a quaternary ammonium surfactant micelle-directed liquid-interface assembly strategy to prepare monodispersed chloropropyl functionalized mesoporous organosilica nanosphere supports (PrCl-MONSs), and the particle size and pore morphology of the supports are well-adjusted by changing the cations and/ or anions of the surfactants as well as the preparation conditions. After successive chemical modification of the 1,3-propanesultone supports with imidazole, and trifluoromethane sulfonic acid (HOTf), monodispersed [C3-PrIm [OTf]-MONSs catalysts with different particle sizes and pore morphologies are successfully achieved. As-prepared [C₃-PrIm [OTf]-MONSs serve as nanoreactors to accommodate efficient and selective conversion of HMF to EL and LA in ethanol and water media, respectively, and the particle sizeand pore morphology-dependent catalytic activity and selectivity are studied at an appropriate reaction temperature and ethanol/water-to-HMF molar ratio. It is found that the high reactivity and selectivity of the [C3PrIm][OTf]-MONSs catalysts in both target reactions are dominated by the combination of superstrong Brønsted acidity, spherical nanostructures with abundant mesopores and surface hydrophobicity. Finally, the catalytic reusability and stability of the [C₃PrIm][OTf]-MONSs are evaluated.

2. Experimental section

2.1. Catalyst preparation

Four quaternary ammonium surfactants with the same hydrophobic chain length (hexadecyl groups) but different counterions including cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), cetylpyridinium bromide (CPB) and cetyltrimethylammonium tosylate (CTATOS) are selected to prepare four *Pr*Cl-MONSs supports including *CTAB Pr*Cl-MONSs, *CTAC Pr*Cl-MONSs, *CPB Pr*Cl-MONSs and *CTATOS Pr*Cl-MONSs. Subsequent functionalization of the supports with BAILs gave rise to four [C₃PrIm][OTf]-MONSs**x** catalysts, where x = 6, 12 and 24, referring to the hydrolysis time of organosilica precursors of 6, 12 and 24 h, as described in the ESI.†

2.2. Characterization of the [C₃PrIm][OTf]-MONSs catalysts

Transmission electron microscopy (TEM) images were obtained by using a JEM-2100F high resolution transmission electron microscope at an accelerating voltage of 200 kV. Field emission scanning electron microscopy (FESEM) images were collected using an XL-30 ESEMFEG field emission scanning electron microscope. Nitrogen gas porosimetry measurements were performed on a Micromeritics ASAP 2020M surface area and porosity analyzer after the samples were calcined at 393 K in a vacuum for 2 h, and outgassed under vacuum at 393 K for another 12 h. The surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation, while pore diameter distribution curves were calculated using the Barrett–Joyner–Halenda (BJH) desorption branch of the isotherms, and the pore volume was accumulated up to $P/P_0 = 0.99$. X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra DLD instrument with a monochromated Al-Kα source at a residual gas pressure below 10^{-8} Pa, and all the binding energies were referenced to the C 1s peak at 284.8 eV of surface adventitious carbon. ¹³C cross polarization-magic angle spinning (CP-MAS) NMR and ²⁹Si MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probe head. The dried and finely powdered samples were packed in a ZrO₂ rotor closed with a Ke–F cap and were spun at a 12 KHz rate.

The Brønsted acid strength of the as-prepared [C₃PrIm] [OTf]-MONSs catalysts was measured using a WDDY-2008] microcomputer potentiometric automatic titration instrument, and the procedure followed has been previously reported.³⁹ 50 mg of sample was suspended in acetonitrile and stirred for 3 h, and then the suspension was titrated with a 0.1 mol L^{-1} solution of *n*-butylamine in acetonitrile. The initial electrode potential (E_i, mV) indicated the maximum acid strength of the surface sites. The Brønsted acid site densities (A, $\mu eq g^{-1}$) of the catalysts were determined by acid-base titration with a NaOH solution.40 Typically, the sample (50 mg) was added into a NaCl solution (10 mL, 2 mol L^{-1}) and continually stirred at room temperature for 24 h. Then, the acid amount in the solution was determined by titration with a NaOH $(0.0044 \text{ mol } \text{L}^{-1})$ standard solution, and therefore the Brønsted acid site density of the tested sample can be calculated.

2.3. Catalytic tests

2.3.1. The synthesis of EL from the ethanolysis of HMF. The ethanolysis reaction was carried out in an autoclave under the conditions: 120°C, an ethanol (EtOH, 69 mmol)-to-HMF (0.278 mmol) molar ratio of 248 and HMF-to-catalyst weight ratio of 1 wt/wt. The concentrations of HMF, 5-ethoxymethylfurfural (EMF) and EL were monitored using a Shimadzu 2014C gas chromatograph (GC) equipped with an HP-INNOWAX capillary column and a flame ionization detector, and ethyl laurate was applied as an internal standard.

2.3.2. The synthesis of LA from the hydrolysis of HMF. The hydrolysis reaction was conducted in an autoclave under the conditions: 140 °C, a water (166.7 mmol)-to-HMF (0.4 mmol) molar ratio of 417 and 1% catalyst (with respect to the total reactants). The concentrations of HMF and LA were simultaneously analyzed using an Agilent Technologies 1260HPLC equipped with a PrevailTM Organic Acid column and an evaporative light-scattering detector (Alltech ELSD 2000ES).

The catalytic performance was evaluated quantitatively by conversion (*Conv*, %), yield (*Y*, %) and selectivity (*Sel*, %), respectively.

The generated intermediates and by-products during the above two reaction processes were identified by both GC-MS

(HP6890GC-5973MSD) and LC-MS (Agilent 1260HPLC-6490 LC/QQQ/Thermo Scientific LTQ-Orbitrap XL), while the concentration of formic acid (by-product of the HMF hydrolysis reaction) was determined using a Metrohm Eco ion chromatograph (IC).

3. Results and discussion

3.1. Fabrication and characterization of the [C₃PrIm][OTf]-MONSs catalysts with tunable particle sizes and pore morphologies

Fabrication of the monodispersed [C₃PrIm][OTf]-MONSs catalysts includes a liquid-interface assembly strategy to prepare chloropropyl functionalized mesoporous organosilica nanosphere supports (PrCl-MONSs) followed by chemical modification with imidazole, 1,3-propanesultone and HOTf successively. At first, the PrCl-MONSs supports are prepared by a quaternary ammonium surfactant micelle-directed sol-gel chemistry process. In order to adjust the particle sizes and pore morphologies of the supports, four quaternary ammonium surfactants (serving as a structure-directing agent, SDA) such as CTAB, CTAC, CPB and CTATOS are selected, leading to CTAB PrCl-MONSs, CTAC PrCl-MONSs, CPB PrCl-MONSs and CTATOS PrCl-MONSs, respectively. As illustrated in Scheme 1, in the initial stage of preparation of the support, SDA self-assembles into monodispersed spherical micelles with an orderly arrangement of hydrophobic chains inside the EtOH-waterenvironment. After slowly NH₄OH dropping an organoalkoxysilane precursor 1,2-bis(trimethoxysilyl)ethane 3-chloropropyltrimethoxysilane (BTMSE) and (CPTMS)containing cyclohexane solution to the above surfactantcontaining colloidal solution, co-hydrolysis and cocondensation of BTMSE and CPTMS in the as-formed weakly alkali O/W microemulsion system occur, which creates strongly



Scheme 1 Morphological evolution and wall structure of the $[C_3PrIm]$ [OTf]-MONSs catalysts.

negatively charged polysilicates at the O/W liquid interface. Co-assembly of these polysilicates with the spherical SDA cation micelles via electrostatic interactions leads to polysilicate-SDA supramolecule aggregates around the outside of the spherical SDA micelles. Continuous stirring of the microemulsion followed by hydrothermal treatment results in slow extension of the supramolecule aggregates along the direction of the hydrophobic chains, which provides a prerequisite for the generation of centrally radialized mesoporous structure within the spherical organosilica support; meanwhile, as-formed Si-C-C-Si-O-Si-PrCl framework is further strengthened. After extraction of SDA from spherical supramolecule aggregates with boiling ethanol, monodispersed mesoporous PrCl-MONSs supports are subsequently fabricated. In the above preparation process, co-hydrolysis and co-condensation of BTMSE and CPTMS happen in a weakly alkali O/W microemulsion system at a suitable cyclohexane-to-EtOH molar ratio, which can control the co-hydrolysis and co-condensation rates of BTMSE and CPTMS in a favorable manner. Accordingly, individual chloropropyl functionalized mesoporous organosilica nanospheres are facilely constructed. Afterwards,

the *Pr*Cl-MONSs are modified with imidazole to yield imidazole modified supports (*Pr*Im-MONSs), accompanied with the release of HCl molecules. Through further quaternary ammonization of *Pr*Im-MONSs with 1,3-propane sultone and then protonation with HOTf, the [C₃PrIm][OTf]-MONSs are ultimately obtained.

The TEM images shown in Fig. 1a and b clearly reveal that the representative support, CTAB PrCl-MONSs12, exhibits monodispersed spherical nanostructures with an average particle size of 270 nm (Table 1), in which periodic centrally radialized mesopores are full of nanospheres. After functionalization of the CTAB PrCl-MONSs12 support with [C3-PrIm [OTf] groups, the resulting CTAB [C₃PrIm][OTf]-MONSs12 can well retain the mesoporous spherical catalyst nanostructures of the support; moreover, the catalyst possesses the same particle size as that of the support (Fig. 1c and d). As for the CTAC [C₃PrIm][OTf]-MONSs12 (Fig. 1e and f) and CPB [C₃PrIm][OTf]-MONSs12 (Fig. 1g and h) catalysts, they display the same monodispersed spherical nanostructures and pore morphologies as those of the CTAB [C₃PrIm][OTf]-MONSs12; however, their particle sizes are different (350 and 260 nm for CTAC [C₃PrIm][OTf]-MONSs12 and CPB [C₃PrIm][OTf]-



Fig. 1 TEM images of CTAB PrCl-MONSs12 (a and b), CTAB [C₃PrIm][OTf]-MONSs12 (c and d), CTAC [C₃PrIm][OTf]-MONSs12 (e and f), CPB [C₃PrIm][OTf]-MONSs12 (g and h), CTATOS [C₃PrIm][OTf]-MONSs12 (i and j), CTAB [C₃PrIm][OTf]-MONSs6 (k and l), CTAB [C₃PrIm][OTf]-MONSs24 (m and n), and CTAB PrSO₃H-MONSs12 (o and p).

Table 1	Brønsted	acid site	e density	(A), in	tial electrode	potential	l (E _i),	average	particle	size (d),	pore	diameter	(D _p),	BET	surface	area	(S _{BET})	and pore
volume (V_p) of the CTAB PrCI-MONSs support, various [C ₃ PrIm][OTf]-MONSs catalysts and reference acid catalyst																		

Catalyst	<i>d</i> (nm)	$D_{\rm p}~({\rm nm})$	$S_{\rm BET} \left({{m}^2 { m{ g}^{ - 1}}} ight)$	$V_{\rm p} ({\rm cm}^3 {\rm g}^{-1})$	$A (\mu eq g^{-1})$	$E_{\rm i}$ (mV)
CTAB PrCl-MONSs12	270	3.3	915	0.90	n.d.	n.d.
CTAB [C ₃ PrIm][OTf]-MONSs6	180	3.2	553	0.64	873	456.1
CTAB [C ₃ PrIm][OTf]-MONSs12	270	3.2	538	0.58	865	424.9
CTAB [C ₃ PrIm][OTf]-MONSs24	360	3.0	433	0.45	792	412.8
CTAC [C ₃ PrIm][OTf]-MONSs12	350	2.9	258	0.24	675	412.6
CPB [C ₃ PrIm][OTf]-MONSs12	260	3.3	537	0.54	865	510.4
CTATOS [C ₃ PrIm][OTf]-MONSs12	210	3.8	581	1.13	880	545.5
CTATOS [C ₃ PrIm][OTf]-MONSs12 3rd ^a	210	3.8	551	0.94	873	n.d.
CTAB PrSO ₃ H-MONSs12	270	3.2	564	0.50	704	340.3
^{<i>a</i>} The catalyst was used for the third time.						

MONSs12, Table 1). Interestingly, CTATOS [C₃PrIm][OTf]-MONSs12 exhibits monodispersed spherical nanostructures but with a wormhole-like interconnected mesoporous structure; additionally, its particle size (210 nm) is the smallest among those of the as-prepared four [C₃PrIm][OTf]-MONSs catalysts (Fig. 1i and j). The results suggest that the anion size and structures of SDAs influence not only the particle size but also the pore morphology of the [C₃PrIm][OTf]-MONSs catalysts. CTATOS and CTAC with the largest and smallest anion (MePhSO₃⁻ and Cl⁻) size can lead to CTATOS [C₃PrIm][OTf]-MONSs12 and CTAC [C3PrIm][OTf]-MONSs12 with the smallest and largest particle sizes; in the cases of CPB [C3PrIm][OTf]-MONSs12 and CTAB [C3PrIm][OTf]-MONSs12 prepared with SDAs with the same anion (Br), their particle sizes are very close. This is due to the fact that the larger anion size of the SDA may limit the growth of polysilicate-SDA supramolecules, leading to a smaller particle size of the [C₃PrIm][OTf]-MONSs. Additionally, during the process of the synthesis of CTATOS PrCl-MONSs, the hydrophobic chains of CTATOS twist together with large-sized MePhSO₃⁻ ions inside the micelles, which causes a twisted and short rod-like arrangement of hydrophobic groups of CTATOS and thus finally results in CTATOS [C₃PrIm] [OTf]-MONSs12 with а wormhole-like interconnected mesostructure. Different from CTATOS PrCl-MONSs, during the process of the synthesis of CTAB-, CTAC- and CPB-directed MONSs, SDA micelles can offer an ordered and stretched arrangement of hydrophobic groups, which ultimately leads to CTAB-, CTAC- and CPB-directed [C3PrIm][OTf]-MONSs with a periodic centrally radialized mesostructure.

To study the influence of co-hydrolysis and co-condensation time of organoalkoxysilane precursors on the pore morphology and particle size of the $[C_3PrIm][OTf]$ -MONSs catalysts, *CTAB* $[C_3PrIm][OTf]$ -MONSs6 and *CTAB* $[C_3PrIm][OTf]$ -MONSs24 are prepared. As shown in Fig. 1k–n, both catalysts present the same monodispersed spherical nanostructures and pore morphologies as those of the *CTAB* $[C_3PrIm][OTf]$ -MONSs12 but different particle sizes (180 and 360 nm for *CTAB* $[C_3PrIm][OTf]$ -MONSs6 and *CTAB* $[C_3PrIm][OTf]$ -MONSs24, Table 1). The result indicates that the co-hydrolysis and co-condensation time of organoalkoxysilane precursors has little influence on the morphology of the $[C_3PrIm][OTf]$ -MONSs catalysts; however, prolonging the co-hydrolysis and co-condensation time can facilitate the growth of the polysilicate–SDA supramolecule aggregates, thereby enlarging the diameter of the *Pr*Cl-MONSs support, which finally gives rise to a larger particle size of the $[C_3PrIm][OTf]$ -MONSs catalyst.

CTAB $PrSO_3H$ -MONSs12, prepared by a similar route to that of *CTAB* [C₃PrIm][OTf]-MONSs12, exhibits the same spherical nanostructure and pore morphology as well as particle size with the latter, further confirming the reproducibility of the preparation method (Fig. 10 and p).

FESEM results of the support (Fig. 2a), [C₃PrIm][OTf]-MONSs catalysts (Fig. 2b-g) and CTAB PrSO₃H-MONSs12 coincide exactly with those from TEM (Fig. 2h) observations, further confirming their monodispersed spherical nanostructures with plentiful mesopores. Moreover, the surface of CTATOS [C3PrIm][OTf]-MONSs12 (Fig. 2g) is more open in comparison to those of the other three catalysts. Additionally, the particle size distributions of the four [C₃PrIm][OTf]-MONSs12 catalysts (Fig. S1a'-d'⁺) are also provided according to FESEM observations (Fig. S1a-d[†]). For CTAB [C₃PrIm][OTf]-MONSs12, CTAC [C₃PrIm] [OTf]-MONSs12, CPB [C₃PrIm][OTf]-MONSs12 and CTATOS [C₃PrIm][OTf]-MONSs12, their particle sizes mainly center at ca. 270, 350, 260 and 210 nm, respectively. The result confirms the uniformity of the as-prepared [C₃PrIm][OTf]-MONSs catalysts.



Fig. 2 FESEM images of CTAB PrCl-MONSs12 (a), CTAB [C_3PrIm][OTf]-MONSs6 (b), CTAB [C_3PrIm][OTf]-MONSs12 (c), CTAB [C_3PrIm][OTf]-MONSs24 (d), CTAC [C_3PrIm][OTf]-MONSs12 (e), CPB [C_3PrIm][OTf]-MONSs12 (f), CTATOS [C_3PrIm][OTf]-MONSs12 (g) and CTAB PrSO_3H-MONSs12 (h).

The interesting monodispersed mesoporous spherical nanostructures of the [C₃PrIm][OTf]-MONSs catalysts give them excellent textural properties. As shown in Fig. S2a and c,† the CTAB PrCl-MONSs12 support and various [C₃PrIm] [OTf]-MONSs catalysts all exhibit a type IV isotherm, reflecting that they possess mesoporous structures; however, their pore-condensation steps appear in different relative pressure (P/P_0) ranges, which is related to their pore morphologies. For CTAB PrCl-MONSs12, CTAB [C3PrIm][OTf]-MONSs12, CTAC [C₃PrIm][OTf]-MONSs12, CPB [C₃PrIm][OTf]-MONSs12 and CTAB PrSO3H-MONSs12 with a periodic pore morphology, their pore-condensation step happens around the range of $P/P_0 = 0.4-0.6$, while the pore-condensation step occurs at $P/P_0 = 0.4-0.8$ for CTATOS [C₃PrIm][OTf]-MONSs12 with an interconnected pore morphology. The results indicate that CTATOS [C₃PrIm][OTf]-MONSs12 has a larger pore diameter than the other catalysts. The BJH pore size distribution curves displayed in Fig. S2b and d† suggest that all tested samples show a sharp pore size distribution, suggesting that the mesopores within the nanospheres are uniform.

From the determined textural parameters based on nitrogen sorption isotherms, it is found that the CTAB PrCl-MONSs12 support possesses a large BET surface area (915 $m^2 g^{-1}$) and high pore volume (0.90 cm³ g⁻¹), contributed by well-defined mesostructures (Table its 1). After functionalization, the resulting CTAB [C₃PrIm][OTf]-MONSs12 shows a decreased BET surface area (538 m² g⁻¹) and pore volume (0.58 cm³ g⁻¹); additionally, the pore diameter of CTAB [C₃PrIm][OTf]-MONSs12 (3.2 nm) decreases slightly in comparison to that of CTAB PrCl-MONSs12 (3.3 nm). The above results confirm that most of the [C₃PrIm][OTf] groups are immobilized on the internal surface of the nanospheres, which leads to the decreased BET surface area and pore volume as well as somewhat blocked pore channels. For the three CTAB [C₃PrIm][OTf]-MONSs catalysts, their BET surface areas and pore volumes decrease gradually with increasing hydrolysis time from 6 to 12 and 24 h (Table 1), originating from the gradually enlarged particle sizes. Finally, the four different surfactant-directed catalysts follow the pore diameter, BET surface area and pore volume order CTATOS $[C_3PrIm][OTf]$ -MONSs12 (3.8 nm, 581 m² g⁻¹, 1.13 cm³ g⁻¹) > *CPB* $[C_3PrIm][OTf]$ -MONSs12 (3.3 nm, 537 m² g⁻¹, 0.54 $\text{cm}^3 \text{g}^{-1}$) $\approx CTAB [C_3 \text{PrIm}][OTf]-MONSs12$ (3.2 nm, 538 $m^2 \ g^{-1}, \ 0.58 \ cm^3 \ g^{-1}) \ > \ \textit{CTAC} \ [C_3 PrIm] [OTf]-MONSs12 \ (2.9 \ cm^2) \ (2.9 \ cm^2)$ nm, 285 m² g⁻¹, 0.24 cm³ g⁻¹). In the case of CTAB $PrSO_3H$ -MONSs12, it has similar textural parameters to those of its CTAB [C₃PrIm][OTf]-MONSs12 counterpart. The above results suggest that the textural properties of the [C₃PrIm][OTf]-MONSs catalysts are dominated by their pore morphologies and particle sizes.

XPS surface probe and MAS NMR techniques are applied to confirm the formation of inorganic-organic silica/carbon framework in the $[C_3PrIm][OTf]$ -MONSs catalysts and the immobilization of the $[C_3PrIm][OTf]$ groups within the support. As presented in Fig. 3a, the high resolution C 1s XPS spectra of the four different SDA-directed [C₃PrIm][OTf]-MONSs catalysts are deconvolved into four individual peaks positioned at 284.6, 285.7, 286.7 and 292.4 eV, respectively, corresponding to C-C bonds from bridging ethyl units and propyl groups, C-N, C-O and C-F bonds within the [C₃PrIm] [OTf] groups, respectively.^{41,42} The immobilization of [C₃-PrIm [OTf] groups within the PrCl-MONSs support is further evidenced by the appearance of two characteristic peaks centered at 168.5 and 169.5 eV in the high resolution S 2p XPS spectra (Fig. 3b), attributed to the S $2p_{3/2}$ and S $2p_{1/2}$ states of the PrSO₃H group and OTf anion.³⁴ Additionally, on the basis of the XPS whole spectra of the CTAB-, CTAC-, CPBand CTATOS-directed [C3PrIm][OTf]-MONSs12 catalysts (Fig. S3[†]), the content (At%) of the nitrogen, sulphur and fluorine elements and their corresponding atomic ratios in the catalysts are estimated (Table S1⁺). As expected, the determined atomic ratios of N:S:F in the four [C₃PrIm][OTf]-MONSs12 catalysts are very close to the stoichiometric ratio (2:2:3) of the parent ionic liquid (Scheme 1). Therefore, the [C₃PrIm][OTf] groups are successfully incorporated into the silica framework without inducing structural changes.

MAS NMR analysis can further support the above results. As shown in Fig. 3c, three characteristic resonance signals at -61.6, -66.7 and -73.7 ppm are detected in the ²⁹Si NMR MAS spectrum of *CTAB* [C₃PrIm][OTf]-MONSs12, and they are assigned to organosilica species including T¹ [C-Si(OSi) $(OH)_2$, T² [C-Si(OSi)₂(OH)] and T³ [C-Si(OSi)₃]. These organosilica species come from co-hydrolysis and cocondensation of organoalkoxysilane precursors (BTMSE and CPTMS), and they construct the silica/carbon framework of the [C₃PrIm][OTf]-MONSs catalysts.⁴³⁻⁴⁵ More abundant structural information concerning the formation of chloropropyl functionalized silica/carbon frameworks (Si-C-C-Si-O-Si-PrCl) and the immobilization of the [C₃PrIm][OTf] groups within the silica/carbon frameworks are provided by the ¹³C CP-MAS NMR spectra of CTAB PrCl-MONSs12, CTAB PrIm-MONSs12 and CTAB [C₃PrIm][OTf]-MONSs12. As shown in Fig. 3d, four carbon species (C^1-C^4) are identified in the CTAB PrCl-MONSs12 support. Specifically, the strongest peak positioned at 5.2 ppm is assigned to carbon species (C^1) of bridging ethyl units of the silica/carbon framework, while the other three peaks centered at 10.1 (C²), 26.3 (C³) and 45.7 ppm (C⁴) are attributed to carbon species from the chloropropyl group.32,46-48 In the case of CTAB PrIm-MONSs12, the aforementioned C^1-C^4 species still can be found, accompanied with the appearance of two new and weak peaks positioned at 120.1 (C^5) and 135.1 ppm (C^6) . The C^5 and C^6 species originate from the imidazole unit, and therefore, the imidazole group is successfully incorporated into the silica/carbon framework to form -Si-C-C-Si-O-Si-PrIm linkage.^{32,48} As for CTAB [C₃PrIm][OTf]-MONSs12, the C¹-C⁶ species originated from the imidazole-functionalized silica/carbon framework remaining intact; meanwhile, two weak peaks emerged at 51.9 (C7) and 122.4 ppm (C8), and they are derived from the -PrSO₃H group covalently bonded to an imidazole cation and the introduced OTf anion,



Fig. 3 High resolution XPS spectra of the different SDA-directed $[C_3PrIm][OTf]$ -MONSs12 catalysts in the C 1s (a) and S 2p (b) binding energy region. (c) ²⁹Si MAS NMR spectrum of *CTAB* $[C_3PrIm][OTf]$ -MONSs12 and (d) ¹³C CP-MAS NMR spectra of *CTAB* PrCl-MONSs12, *CTAB* PrIm-MONSs12 and *CTAB* $[C_3PrIm][OTf]$ -MONSs12.

respectively.⁴⁹ Therefore, it is evidenced that the $[C_3]$ [OTf] group is successfully bonded to the imidazole-functionalized silica/carbon framework to create the $[C_3PrIm]$ [OTf]-MONSs catalysts. It should be noted that due to the different chemical environments of C³ and C⁴ species in *CTAB Pr*Cl-MONSs12, *CTAB Pr*Im-MONSs12 and *CTAB* [C₃PrIm][OTf]-MONSs12, their chemical shifts have slight differences.

From the combination of XPS and MAS NMR analysis results, we firmly speculate that $[C_3PrIm][OTf]$ functionalized ethyl-bridged organosilica is successfully constructed by using the currently designed liquid-interface assembly strategy followed by further chemical modifications, and they constructed the wall structure of the catalyst, as illustrated in Scheme 1.

The strength of Brønsted acid sites of the $[C_3PrIm][OTf]$ -MONSs catalysts is measured by nonaqueous potentiometric titration with *n*-butylamine in acetonitrile, and the obtained initial electrode potential (E_i) value indicates the maximum acid strength of the surface sites. Generally, a material with an E_i value higher than 100 mV is defined as a very strong solid acid.⁵⁰ As presented in Table 1, the measured E_i values of as-prepared $[C_3PrIm][OTf]$ -MONSs are in the range of 456.1 to 545.5 mV, indicating their superstrong Brønsted acidic nature. The Brønsted acid site density of the $[C_3PrIm][OTf]$ - MONSs are determined by acid-base titration with a dilute NaOH solution. As listed in Table 1, for the three CTAB [C3-PrIm [OTf]-MONSs catalysts with different particle sizes, i.e., CTAB [C₃PrIm][OTf]-MONSs6, CTAB [C₃PrIm][OTf]-MONSs12 and CTAB [C3PrIm][OTf]-MONSs24, their Brønsted acid site density (873, 865 and 792 μ eq g⁻¹) gradually decreases with continuously increasing particle size (180, 270 and 360 nm). In the cases of the four [C₃PrIm][OTf]-MONSs catalysts prepared under the same conditions but using different SDAs, *i.e.*, *CTATOS* [C₃PrIm][OTf]-MONSs12, *CPB* [C₃PrIm] [OTf]-MONSs12, CTAB [C₃PrIm][OTf]-MONSs12 and CTAC [C₃-PrIm [OTf]-MONSs12, the difference among their Brønsted acid site density is also related to the particle size. Specifically, CTATOS [C₃PrIm][OTf]-MONSs12 and CTAC [C₃-PrIm [OTf]-MONSs12 with the smallest and the largest particle size (210 vs. 350 nm) show the highest and the lowest Brønsted acid site density (880 vs. 675 μ eq g⁻¹), while CPB [C₃PrIm][OTf]-MONSs12 and CTAB [C₃PrIm][OTf]-MONSs12 with very close particle sizes (260 and 270 nm) display the same acid site density (865 μ eq g⁻¹). This is due to the fact that the increase of the particle size of the catalyst leads to somewhat a decrease of its BET surface area and pore volume, which results in less exposed surface Brønsted acid sites and thereby a reduced Brønsted acid site density.

3.2. Evaluation of the catalytic performance of the [C₃PrIm] [OTf]-MONSs

3.2.1. Catalytic activity and selectivity. The acid catalytic activity and selectivity of the as-prepared $[C_3PrIm][OTf]$ -MONSs catalysts are evaluated by transformation of HMF to EL and LA in green solvents like EtOH and H₂O media.

The synthesis of EL from the ethanolysis of HMF. As illustrated in Scheme S1a,† the acid-catalyzed transformation of HMF to EL by using EtOH as both the reactant and solvent starts from the protonation of the hydroxymethyl group of HMF. Subsequently, the main intermediate, ethoxymethylfurfural (EMF), is rapidly formed via etherification reaction under the nucleophilic attack of EtOH molecules, accompanied with the release of water molecules (identified by GC-MS, retention time of 9.88 min in Fig. S4[†]). The final formation of EL from EMF is the rate-limiting step, which undergoes multiple steps including nucleophilic addition, dehydration and ring opening.⁵¹ In the search for optimum reaction conditions for the synthesis EL with high yield, the influence of the important experimental parameters such as reaction temperature and EtOH-to-HMF molar ratio on the catalytic activity and selectivity is studied by using CTAB [C3-PrIm [OTf]-MONSs12 as the representative catalyst. Afterwards, the particle size- and pore morphology-dependent activity and selectivity of the [C₃PrIm][OTf]-MONSs in the target reaction are revealed under the optimum reaction conditions.

As presented in Fig. 4a, in the CTAB [C₃PrIm][OTf]-MONSs12-catalyzed ethanolysis of HMF reaction system, the conversion of HMF increases rapidly from 82.4 to 96.8% (120 min) with elevating reaction temperature from 80 to 100 °C, and by further increasing the reaction temperature to 120 and 140 °C, the conversion of HMF reaches 99.9%. Simultaneously, the selectivity of the catalyst to EMF reaches the maximum value (45.6%) at 100 °C, and then it continuously reduces to 23.9% with elevating reaction temperature to 140 °C, whereas the selectivity to EL increases remarkably with the temperature, e.g., from 3.0 to 16.4 and 65.6% at 80, 100 and 120 °C, respectively. By further elevating the reaction temperature to 140 °C, the selectivity to EL has a slight decrease (62.2%). The above results indicate that the transformation of HMF to EL extremely depends on the reaction temperature. Lower reaction temperature (e.g., 80 °C) not only limits the transformation of HMF to EL but also to EMF, while higher reaction temperature (e.g., 120 °C) boosts further transformation of EMF to EL, thus reducing the selectivity to EMF. At a reaction temperature of 140 °C, the slightly decreased selectivity to EL is due to the formation of by-products, e.g., 2,5-bis(furan-2-ylmethyl)furan (identified by GC-MS, retention time of 12.58 min in Fig. S4a[†]) by selfpolymerization of HMF. Therefore, much higher reaction temperature (e.g., 140 °C) can not only promote the conversion of HMF but also facilitate the self-polymerization of HMF to oligomeric by-products, thus decreasing the selectivity to EL. Consequently, the reaction temperature of 120 °C is set for following tests.



Fig. 4 Influence of reaction temperature (a) and $n_{\text{EtOH}}: n_{\text{HMF}}$ ratio (b) on the catalytic activity and selectivity of *CTAB* [C₃PrIm][OTf]-MONSs**12** in ethanolysis of HMF. (a) 0.278 mmol HMF, 69 mmol EtOH, $n_{\text{EtOH}}: n_{\text{HMF}} = 248$, HMF-to-catalyst weight ratio of 1 wt/wt, 120 min; (b) 0.278 mmol HMF, 120 °C, HMF-to-catalyst weight ratio of 1 wt/wt, 120 min.

On the basis of the results displayed in Fig. 4a, the Arrhenius model ($\ln k = \ln k_0 - E_a/RT$) is applied by fitting the formation rate of EL at 80, 100, 120 and 140 °C. As shown in Fig. S5,† the determined activation energy (E_a) is 68.1 kJ mol⁻¹ for the *CTAB* [C₃PrIm][OTf]-MONSs12-catalyzed HMF ethanolysis reaction. According to the literature, if the E_a value is higher than 41.8 kJ mol⁻¹, the HMF ring-opening reaction follows a reaction-limited mechanism.⁵² Therefore, it is more consistent with reaction-limited kinetics rather than diffusion-limited kinetics for the [C₃PrIm][OTf]-MONSs-catalyzed-ethanolysis of HMF reaction, in which the ring-opening step is involved.

At the reaction temperature of 120 °C and reaction time of 120 min, the influence of EtOH-to-HMF molar ratio $(n_{\text{EtOH}}:n_{\text{HMF}})$ on the conversion of HMF and selectivity to EL is studied subsequently. From the result shown in Fig. 4b, it is found that the transformation of HMF is finished at various $n_{\text{EtOH}}:n_{\text{HMF}}$ ratios. Additionally, the selectivity of *CTAB* [C₃PrIm][OTf]-MONSs12 to EL increases apparently from 17.9 to 63.9 and 65.5% with increasing $n_{\text{EtOH}}:n_{\text{HMF}}$ ratio from 124 to 186 and 248; by further increasing the ratio to 310, the selectivity to EL decreases to 58.8%. The selectivity of *CTAB* [C₃PrIm][OTf]-MONSs12 to EMF is relatively low (lower than 25.4%) at $n_{\text{EtOH}}:n_{\text{HMF}}$ ratios of 124, 186, 248 and 310. The above results are

explained below. At a lower $n_{\rm EtOH}$: $n_{\rm HMF}$ ratio (*e.g.*, 124), the reactant HMF has a high concentration, thus creating a favourable condition for the self-polymerization of HMF to oligomeric by-products, *e.g.*, 2,5-bis(furan-2-ylmethyl)furan, with high concentration under the acid catalysis over *CTAB* [C₃PrIm][OTf]-MONSs12, as confirmed by GC-MS (retention time of 12.58 min, Fig. S4b†). As a consequence, the total selectivity of *CTAB* [C₃PrIm][OTf]-MONSs12 to both EL and EMF is relatively low. Otherwise, at a higher $n_{\rm EtOH}$: $n_{\rm HMF}$ ratio (*e.g.*, 310), HMF is diluted significantly, which may decelerate the formation of EMF and EL to some extent. Accordingly, a suitable $n_{\rm EtOH}$: $n_{\rm HMF}$ ratio (*e.g.*, 248) can avoid equilibrium limitation and facilitate the conversion of HMF to EL. In the following tests, the $n_{\rm EtOH}$: $n_{\rm HMF}$ ratio is set at 248.

Under the conditions: 120 °C and n_{EtOH} : n_{HMF} ratio of 248, the particle size- and pore morphology-dependent activity and selectivity of $[C_3PrIm][OTf]$ -MONSs in ethanolysis of HMF to EL are studied. At first, the three *CTAB* $[C_3PrIm]$ [OTf]-MONSs catalysts with different particle sizes (180, 270 and 360 nm) are tested. As shown in Fig. 5a, conversion of HMF occurs rapidly over the three tested *CTAB* $[C_3PrIm]$ [OTf]-MONSs catalysts, regardless of their particle sizes. After the reaction proceeds for 20 min, the conversion of HMF reaches 94.6, 94.3 and 92.4% in *CTAB* $[C_3PrIm]$ [OTf]-MONSs6-, *CTAB* $[C_3PrIm]$ [OTf]-MONSs12- and *CTAB* $[C_3PrIm]$ [OTf]-MONSs24-catalyzed ethanolysis of HMF, respectively. By prolonging the reaction time to 60 min, conversion of HMF is completed. However, the selectivity of *CTAB* $[C_3$ -PrIm][OTf]-MONSs to EL is obviously influenced by the



Fig. 5 Particle size- and morphology-dependent activity (a and c) and selectivity (b and d) of $[C_3PrIm][OTf]$ -MONSs in ethanolysis of HMF. Activity (e) and selectivity (f) of the reference solid acids in the target reaction. n_{EtOH} : n_{HMF} = 248, HMF-to-catalyst weight ratio 1 wt/wt, 120 °C.

reaction time and particle size of the catalysts (Fig. 5b). Specifically, the selectivity of the three CTAB [C₃PrIm][OTf]-MONSs catalysts to EL gradually increases with prolonged reaction time; meanwhile, the selectivity of the catalysts to EMF increases at the initial stage of the reaction, and then it gradually decreases with the reaction time after reaching the peak. The result reflects that HMF can be transformed to EMF quickly over the CTAB [C₃PrIm][OTf]-MONSs; however, further transformation of EMF to EL occurs slowly because it suffers from multiple steps. Additionally, CTAB [C₃PrIm][OTf]-MONSs6 and CTAB [C₃PrIm][OTf]MONSs12 with a smaller particle size (180 and 270 nm) show much higher selectivity to EL rather than EMF in comparison to CTAB [C₃PrIm][OTf]-MONSs24 with a larger particle size (360 nm). For example, the selectivity to EL reaches 92.3 (CTAB [C₃PrIm][OTf]-MONSs6), 90.6 (CTAB [C₃PrIm][OTf]-MONSs12) and 51.0% (CTAB [C₃PrIm][OTf]-MONSs24), respectively, after the ethanolysis reaction proceeds for 240 min; simultaneously, the corresponding selectivity to EMF is 1.0, 1.4 and 18.0%, respectively.

Subsequently, the four different SDA-directed catalysts are compared. As shown in Fig. 5c, the tested catalysts show fast transformation of HMF, and the transformation is finished within 60 min. In the case of the selectivity of the four catalysts to EMF, it increases in the beginning of the ethanolysis reaction, and then it starts to decrease as the reaction time is prolonged (Fig. 5d). Among the four catalysts, CTAC [C3PrIm][OTf]-MONSs12 exhibits the highest selectivity to EMF (68.0%, 60 min); additionally, over a period of 240 min, most of EMF has been transformed to EL under the catalysis of CTAB [C₃PrIm][OTf]-MONSs12, CPB [C₃PrIm] [OTf]-MONSs12 or CTATOS [C3PrIm][OTf]-MONSs12. However, a considerable amount of EMF still exists in the CTAC [C3-PrIm [OTf]-MONSs12-catalyzed reaction system. For example, the selectivity of CTATOS [C₃PrIm][OTf]-MONSs12, CPB [C₃-PrIm][OTf]-MONSs12, CTAB [C3PrIm][OTf]-MONSs12 and CTAC [C₃PrIm][OTf]-MONSs12 to EL is 93.7, 91.4, 90.6 and 48.7%, respectively, at the reaction time of 240 min; simultaneously, the corresponding selectivity to EMF is 1.0, 1.0, 1.4 and 15.0%, respectively.

Under identical experimental conditions, reference solid acid catalysts including CTAB PrSO3H-MONSs12, Amberlyst-15 resin and HY zeolite are also tested for comparison. As shown in Fig. 5e, after the CTAB PrSO₃H-MONSs12-, Amberlyst-15 resin- and HY zeolite-catalyzed ethanolysis reaction proceeds for 20 min, the conversion of HMF is 85.9, 86.2 and 63.7%, respectively. By prolonging the reaction time to 60 min, the transformation of HMF over the reference catalysts is completed. The result implies that the ethanolysis activity of the three reference solid acids is lower than that of as-prepared [C₃PrIm][OTf]-MONSs to different extents. From the result shown in Fig. 5f, it is found that three catalysts show the highest selectivity to EMF at the reaction time of 40 min, which is 59.7 (CTAB PrSO₃H-MONSs12), 57.5 (Amberlyst-15 resin) and 50.5% (HY zeolite), respectively, and then the selectivity to EMF gradually decreases with the reaction time.

Additionally, the three catalysts display continuously increasing selectivity to EL with the reaction time; however, remarkably increased selectivity to EL is only found for Amberlyst-15 resin (76.7%, 240 min), while *CTAB Pr*SO₃H-MONSs12 (30.2%) and HY zeolite (27.6%) exhibit poor selectivity to EL at the reaction time of 240 min. Therefore, except for *CTAC* [C₃PrIm][OTf]-MONSs12 and *CTAB* [C₃PrIm] [OTf]-MONSs24 with a large particle size, the other four asprepared [C₃PrIm][OTf]-MONSs all show obviously higher ethanolysis activity and selectivity to EL, outperforming Amberlyst-15 resin and HY zeolite.

On the basis of the above results, we conclude that the various [C3PrIm][OTf]-MONSs catalysts, regardless of their particle sizes and pore morphologies, all can transform HMF in EtOH media rapidly and completely. The high conversion of HMF over the [C₃PrIm][OTf]-MONSs is mainly dominated by the inherent superstrong Brønsted acidic nature of the catalysts, which can boost the fast transformation of HMF; additionally, the unique spherical morphology of the $[C_3-$ PrIm [OTf]-MONSs with an open surface and 2D periodic or 3D interconnected mesopore channels is readily accessible, and they serve as nanoreactors that are favourable for diffusion and mass transfer of the reactants and products, which leads to the positive influence on the fast transformation of HMF. However, the selectivity of the [C₃-PrIm [OTf]-MONSs to EL is remarkably influenced by the particle sizes and pore morphologies of the catalysts, which finally results in different yields of EL. For example, CTAB [C₃PrIm][OTf]-MONSs6 and CTATOS [C₃PrIm][OTf]-MONSs12 with the smallest particle size (180 and 210 nm) show the highest (92.2 and 93.6%, 240 min) yield of EL, while CTAC [C₃PrIm][OTf]-MONSs12 and CTAB [C₃PrIm][OTf]-MONSs24 with the largest particle size (350 and 360 nm) show the lowest yield of EL (48.7 and 50.9%, 240 min). As for the other two catalysts, CPB [C₃PrIm][OTf]-MONSs12 and CTAB [C₃-PrIm [OTf]-MONSs12, their particle size (260 and 270 nm) and pore morphology are almost the same, and they show the same yield of EL (91.3 and 90.5%, 240 min). The smaller particle size of the mesoporous [C3PrIm][OTf]-MONSs catalysts can shorten the diffusion distance of reactants and products, which favors the reaction kinetics and thereby fast transformation of HMF to the final product EL; meanwhile, the smaller [C₃PrIm][OTf]-MONSs catalyst possesses a larger BET surface area and higher pore volume and thus more exposed acid sites, which can improve the accessibility of the acid sites. This is also one of the important reasons for the acceleration of the transformation of HMF to EL, giving rise to higher selectivity to EL and thus high yield of EL. For the largest CTAB [C₃PrIm][OTf]-MONSs24 and CTAC [C₃PrIm] [OTf]-MONSs12, the increased diffusion distance of reactants and products, and inferior textural properties accompanied with less exposed acid sites obviously slow down the transformation of HMF to EL; as a consequence, they show relatively high selectivity to EMF (or lower selectivity to EL) but low yield of EL. It should be noted that CTATOS [C₃PrIm] [OTf]-MONSs12 possesses a unique open surface and 3D

wormhole-like interconnected mesostructure, which gives it excellent porosity properties including the largest pore diameter, the largest BET surface area and the highest pore volume among the as-prepared six [C₃PrIm][OTf]-MONSs catalysts. All of these advantages give rise to the high exposure degree of the acid sites of CTATOS [C₃PrIm][OTf]-MONSs12 to the reactants; accordingly, it shows the highest ethanolysis activity and selectivity to EL. Amberlyst-15 resin is a superstrong Brønsted acid (E_i value of 617.0 mV)⁵³ with an extremely high Brønsted acid-site density (4800 μ eg g⁻¹),^{11,54} which leads to the considerably fast transformation of HMF to EL. However, the small BET surface area of Amberlyst-15 resin $(50 \text{ m}^2 \text{ g}^{-1})^{11,54}$ results in a low exposure degree of the acid sites to the reactants. Accordingly, Amberlyst-15 resin shows a somewhat slow transformation rate for EL, and at a reaction time of 240 min, a considerable amount of EMF still has not been transformed (selectivity to EMF is 15.1%). Although the particle size and pore morphology of CTAB PrSO₃H-MONSs12 are similar to those of its CTAB [C₃PrIm] [OTf]-MONSs12 counterpart, the relatively weak Brønsted acid strength and lower acid site density make CTAB PrSO3H-MONSs12 have very low selectivity to EL, accompanied with the formation of more by-products such as 5-methylfuran-2carbaldehyde and 2,5-bis(furan-2-ylmethyl)furan (retention time of 5.67 and 12.61 min, detected by GC-MS, Fig. S4c[†]) from the dehydration and self-polymerization of HMF. In the case of HY zeolite, its microporosity with a pore diameter of 0.7 nm (ref. 53) and low Brønsted acid site density (608 µeq g^{-1})⁵³ make it have poor conversion ability for EL, and more by-products are produced in this system (retention time of 5.64 and 12.61 min, detected by GC-MS, Fig. S4d⁺). The above results confirm that the particle size- and morphologycontrolled preparation of the supported BAILs is an effective strategy to improve their catalytic activity and selectivity in transformation of HMF to valuable chemicals such as EL.

Finally, the surface hydrophobicity of the $[C_3PrIm][OTf]$ -MONSs originating from bridging ethyl units within the silica/carbon framework also contributes to the high catalytic activity and selectivity to EL to some extent by preventing the adsorption of hydrophilic by-products such as oligomers and water on the catalyst surface, boosting the transformation of HMF at a fast rate.

The synthesis of LA from the hydrolysis of HMF. As illustrated in Scheme S1b,† the Brønsted acid-catalyzed transformation of HMF to LA in water medium begins from the protonation of the hydroxymethyl group of HMF. Under the attack of water molecules, the protonated HMF undergoes successive dehydration, ring opening, release of formic acid and then formation of the final product (LA). Different from the transformation of HMF in EtOH medium, the transformation of HMF in water media suffers from harsher reaction conditions such as higher temperature, which may lead to more oligomer by-products and thereby low selectivity to LA. Moreover, leaching of BAIL sites may occur due to the solvent effect of water, which provides a stronger polarity and hydrogen bonding, limiting the transformation process of reactant-to-transition product-tofinal product. In order to efficiently and selectively synthesise LA from the hydrolysis of HMF, the influence of important experimental parameters such as reaction temperature, H_2O to-HMF molar ratio and organic solvent on the hydrolysis activity and selectivity to LA is firstly studied by using the most active *CTATOS* [C₃PrIm][OTf]-MONSs12 as the representative catalyst. Subsequently, the influence of particle size and pore morphology on the hydrolysis activity and selectivity to LA is revealed under the optimum reaction conditions.

As presented in Fig. 6a, with increasing reaction temperature, the conversion of HMF increases remarkably. For example, after the *CTATOS* [C₃PrIm][OTf]-MONSs12-catalyzed



Fig. 6 Influence of reaction temperature (a), n_{H_2O} : n_{HMF} ratio (b) and solvent (c) on the catalytic activity and selectivity of *CTATOS* [C₃PrIm] [OTf]-MONSs**12** in hydrolysis of HMF. (a) 0.4 mmol HMF, 166.7 mmol H₂O, 120 min; (b) 0.4 mmol HMF, 140 °C, 120 min; (c) 0.4 mmol HMF, 2 mL organic solvents and 1 mL H₂O mixture, 140 °C, 30 mg catalyst, 120 min.

HMF hydrolysis reaction proceeds for 120 min, the conversion of HMF reaches 32.7 (100 °C), 35.7 (120 °C), 74.1 (140 °C) and 99.9% (160 °C), respectively; additionally, the highest selectivity of the catalyst to LA (82.2%) is achieved at 140 °C, and by further increasing the temperature to 160 °C, the selectivity to LA (73.1%) decreases. The decreased selectivity to LA at 160 °C is due to the formation of more oligomer by-products such as 5,5'-oxybis(methylene)difuran-2-carbaldehyde (m/z = 235) via etherification reaction of two molecules of HMF and (5-formylfuran-2-yl)methyl 4-oxopentanoate (m/z = 225) via esterification reaction of HMF with LA (identified by LC-MS analysis, Fig. S6a and b⁺). Therefore, in order to ensure a considerably rapid HMF hydrolysis rate and avoid the formation of a high concentration of oligomer by-products simultaneously, the optimum hydrolysis temperature of 140 °C is set in the subsequent catalytic tests.

Next, at 140 °C and 120 min, the influence of the H₂O-to-HMF molar ratio $(n_{H_2O}: n_{HMF})$ on the HMF hydrolysis activity and selectivity of CTATOS [C3PrIm][OTf]-MONSs12 is studied. As displayed in Fig. 6b, the conversion of HMF approaches 100% at a lower $n_{\rm H_2O}$: $n_{\rm HMF}$ ratio (139 and 278), and by increasing the ratio to 417 and 556, the conversion decreases to 74.4 and 57.9%, respectively. This is due to the fact that a lower $n_{H,O}$: n_{HMF} ratio or higher HMF concentration can significantly facilitate the transformation of HMF at a fast rate. As for the selectivity to LA, it continuously increases from 39.5 to 80.9% with increasing $n_{\rm H_2O}$: $n_{\rm HMF}$ ratio from 139 to 556. The reason for this is that a higher $n_{\rm H_2O}$: $n_{\rm HMF}$ ratio or lower HMF concentration can inhibit the selfpolymerization of HMF to oligomer by-products. Therefore, considering the fast and selective transformation of HMF to LA, in subsequent catalytic tests, the $n_{H,O}$: n_{HMF} ratio is set at 417.

Solvent is one of the key parameters that influences HMF hydrolysis activity and selectivity to LA. Here, at an organic solvent (THF, DMSO or acetone)-to-H₂O volume ratio of 2, 140 °C and 120 min, the conversion of HMF and selectivity to LA in the *CTATOS* [C₃PrIm][OTf]-MONSs12 system is studied. As displayed in Fig. 6c, the highest hydrolysis activity and selectivity to LA occur in a pure water system, and in the presence of an organic solvent, both the conversion of HMF and selectivity to LA decrease remarkably. For example, the conversion of HMF and selectivity to LA are 74.1% and 82.2% (water), 53.3% and 36.2% (acetone-H2O), 43.0% and 62.1% (DMSO-H₂O) and 29.4% and 25.9% (THF-H₂O). Therefore, the selectivity to LA is related to the polarity of the solvent, and HMF and H₂O with the weakest and strongest polarity show the lowest and highest selectivity to LA. This is due to the fact that the strong polarity of H₂O can promote the release of H⁺ from the [C₃PrIm][OTf] group, leading to rapid transformation of HMF to LA. Additionally, LA is highly soluble in water. Therefore, H₂O as both reactant and solvent is chosen for the HMF hydrolysis reaction.

Under the conditions: 140 °C, an n_{H_2O} : n_{HMF} molar ratio of 417 and water medium, the HMF hydrolysis activity and selectivity of the four different SDA-directed catalysts are also compared. As displayed in Fig. 7a, the conversion of HMF obviously increases with prolonged reaction time; additionally, similar to their activity trend for the HMF ethanolysis reaction, CTATOS [C3PrIm][OTf]-MONSs12 and CTAC [C3PrIm][OTf]-MONSs12 also exhibits the highest and lowest activity in the HMF hydrolysis reaction among the four tested [C₃PrIm][OTf]-MONSs catalysts, while CTAB [C₃PrIm] [OTf]-MONSs12 and CPB [C3PrIm][OTf]-MONSs12 show similar hydrolysis activity. After the HMF hydrolysis reaction proceeds for 240 min, the conversion of HMF reaches 99.9 (CTATOS [C₃PrIm][OTf]-MONSs12), 92.4 (CPB [C₃PrIm][OTf]-MONSs12), 87.2 (CTAB [C₃PrIm][OTf]-MONSs12) and 81.8% (CTAC [C₃PrIm][OTf]-MONSs12), respectively. Under the same conditions, the hydrolysis activity of Amberlyst-15 resin (conversion of HMF is 99.9%) is comparable to that of the most active CTATOS [C3PrIm][OTf]-MONSs12; however, HY zeolite shows the lowest conversion of HMF (63.9%).

As displayed in Fig. 7b, the selectivity of [C₃PrIm][OTf]-MONSs12 and the reference catalysts to LA reaches the highest value when the HMF hydrolysis reaction is performed for 120 min, and the corresponding selectivity is 82.2 (*CTATOS* [C₃PrIm][OTf]-MONSs12), 73.1 (*CPB* [C₃PrIm][OTf]-MONSs12), 71.5 (*CTAB* [C₃PrIm][OTf]-MONSs12), 66.7 (*CTAC* [C₃PrIm][OTf]-MONSs12), 56.1 (Amberlyst-15 resin) and 82.6% (HY zeolite), respectively. By extending the reaction time to 240 min, the selectivity decreases to some extent,



Fig. 7 Catalytic activity (a) and selectivity (b) comparison of the various SDA-directed [C₃PrIm][OTf]-MONSs catalysts and the reference solid acids in HMF hydrolysis reactions. $n_{\rm H_2O}$: $n_{\rm HMF}$ = 417, 30 mg catalyst, 140 °C.

Similar to the ethanolysis testing results, the above results further confirm that the superstrong Brønsted acidic nature of the [C₃PrIm][OTf]-MONSs catalysts can accelerate the transformation of HMF in water media to LA, leading to high conversion of HMF; additionally, the particle sizes and pore morphologies of the catalysts influence the hydrolysis activity and selectivity remarkably. CTATOS [C3PrIm][OTf]-MONSs12 with the smallest particle size, largest pore diameter, largest BET surface area, highest pore volume and 3D wormhole-like interconnected mesostructure shows high accessibility of the acid sites to the reactants; accordingly, it also shows the highest hydrolysis activity and selectivity to LA and thus the highest LA yield among the four tested [C3PrIm][OTf]-MONSs12 catalysts. For example, the yield of LA reaches 72.8% after the CTATOS [C3PrIm][OTf]-MONSs12-catalyzed HMF hydrolysis reaction proceeds for 240 min under the reaction conditions listed in Fig. 7. In the case of Amberlyst-15 resin, its superstrong Brønsted acidic nature and high acid site density lead to high hydrolysis activity; however, its low exposure degree of the acid sites to the reactants may limit the transformation of HMF to the final product (LA). HY zeolite catalyzing the HMF hydrolysis reaction possesses relatively low catalytic activity but high selectivity to LA. This is due to the microporous structure of HY zeolite possibly retarding the esterification reaction between HMF molecules and LA because the produced bulky oligomeric by-products are hardly formed within the micropores (confirmed by LC-MS analysis, Fig. S6d†). Similar to ethanolysis of HMF, the HY zeolite-catalyzed hydrolysis of HMF also produces some oligomeric by-products from self-polymerization of HMF on the surface of the catalyst.

The carbon balances in CTATOS [C3PrIm][OTf]-MONSs12catalyzed ethanolysis and hydrolysis of HMF have been provided by taking into account the products, intermediates and by-products under the optimal conditions. As shown in Scheme S2a,[†] for the CTATOS [C₃PrIm][OTf]-MONSs12catalyzed HMF ethanolysis reaction performed under the conditions: n_{EtOH}: n_{HMF} molar ratio of 248, 120 °C and 240 min, HMF (Conv = 99.9%) is transformed to product EL (Y_{EL} = 93.6%), intermediate EMF ($Y_{\rm EMF}$ = 1%) and by-products including 2,5-bis(furan-2-ylmethyl)furan (identified by GC-MS, Fig. S4[†]) as well as a small amount of humins. The carbon balance is therefore 94.6% in CTATOS [C3PrIm][OTf]-MONSs12-catalyzed ethanolysis of HMF under the given reaction conditions. As shown in Scheme S2b,† in the CTATOS [C3PrIm][OTf]-MONSs12-catalyzed hydrolysis of HMF performed at an $n_{\rm H_2O}$: $n_{\rm HMF}$ molar ratio of 417, 140 °C and 240 min, HMF (Conv = 99.9%) is transformed to product LA $(Y_{\text{LA}} = 72.8\%)$, by-products including formic acid (FA, $Y_{\text{FA}} =$ 8.6%), oligomers like 5,5'-oxybis(methylene)difuran-2carbaldehyde and (5-formylfuran-2-yl)methyl 4-oxopentanoate (identified by LC-MS, Fig. S6c†) and a small amount of humins. The carbon balance is therefore 72.8% in CTATOS

 $[C_3PrIm][OTf]$ -MONSs12-catalyzed hydrolysis of HMF under the given reaction conditions. Therefore, the synthesis of EL/ LA over the $[C_3PrIm][OTf]$ -MONSs with high selectivity and high yield can be achieved by complete conversion of HMF, and thus humin formation is a minor pathway.

The turnover frequency (TOF) accounts for differences in acid site density by normalizing the EL and LA formation rate by the number of Brønsted acid sites on each catalyst. As displayed in Fig. 8, in the HMF ethanolysis reaction, the tested catalysts follow the TOF value order CTATOS [C₃PrIm] [OTf]-MONSs12 (67.5 × 10⁻³ min⁻¹) > CPB $[C_3PrIm][OTf]$ -MONSs12 $(57.7 \times 10^{-3} \text{ min}^{-1}) > CTAB [C_3 PrIm][OTf]-MONSs12$ $(54.5 \times 10^{-3} \text{ min}^{-1}) > CTAC [C_3PrIm][OTf]-MONSs12 (35.6 \times 10^{-3} \text{ min}^{-1}) > CTAC [C_3PrIm][OTf] + CTAC [C_3P$ 10^{-3} min^{-1}) > CTAB PrSO₃H-MONSs12 (25.4 × 10^{-3} min^{-1}) > HY zeolite $(15.7 \times 10^{-3} \text{ min}^{-1})$ > Amberlyst-15 resin $(6.1 \times 10^{-3}$ min⁻¹); as for HMF hydrolysis reaction, they follow the TOF value order CTATOS [C₃PrIm][OTf]-MONSs12 (75.5 \times 10⁻³ \min^{-1}) > CPB [C₃PrIm][OTf]-MONSs12 (64.2 × 10⁻³ min⁻¹) > *CTAC* $[C_3PrIm][OTf]-MONSs12$ (62.6 × 10⁻³ min⁻¹) > HY zeolite (61.8 \times 10⁻³ min⁻¹) > CTAB [C₃PrIm][OTf]-MONSs12 $(58.6 \times 10^{-3} \text{ min}^{-1}) > \text{Amberlyst-15 resin} (7.0 \times 10^{-3} \text{ min}^{-1}).$ Therefore, CTATOS [C₃PrIm][OTf]-MONSs12 still performs the best in the synthesis of EL and LA from ethanolysis and hydrolysis of HMF as revealed by the TOF values.

To further evaluate the catalytic performance of the $[C_3$ -PrIm][OTf]-MONS catalysts, sugars as the substrates are also



Fig. 8 Catalytic activity comparison of various [C₃PrIm][OTf]-MONSs and reference solid acids in ethanolysis (a) and hydrolysis (b) of HMF revealed by TOF_{EL} and TOF_{LA} values (min⁻¹), respectively. (a) n_{EtOH} : n_{HMF} = 248, HMF-to-catalyst weight ratio of 1 wt/wt, 120 °C, 40 min; (b) $n_{\text{H}_{2}\text{O}}$: n_{HMF} = 417, 30 mg catalyst, 140 °C, 60 min.

applied in the synthesis of EL/LA over CTATOS [C₃PrIm][OTf]-MONS12. As shown in Fig. S7a,† in the ethanolysis of sugar reactions, the conversion of sugar over CTATOS [C₃PrIm] [OTf]-MONS12 reaches 98.1 (fructose), 94.7 (glucose) and 96.3% (sucrose), respectively, over a period of 240 min; meanwhile, the selectivity of the catalyst to EL is 74.6 (fructose), 21.5 (glucose) and 39.3% (sucrose), respectively. In the hydrolysis of sugar reactions, the conversion of sugar to LA in water media over CTATOS [C3PrIm][OTf]-MONS12 reaches 98.0 (fructose), 94.2 (glucose) and 96.8% (sucrose), respectively, over a period of 240 min; meanwhile, the selectivity of the catalyst to LA is 47.8 (fructose), 18.8 (glucose) and 31.6% (sucrose), respectively (Fig. S7b⁺). The result indicates that CTATOS [C3PrIm][OTf]-MONS12 can transform not only HMF but also sugars in EtOH/H₂O media rapidly and completely. The lower selectivity of the catalyst to EL/LA (or lower EL/LA yield) by using sugars as the reactants in comparison to that using HMF is due to the complicated structure of sugars, and therefore the transformation of sugars to EL/LA in EtOH/H2O media suffers from a more complex process, accompanied with the production of more by-products. Additionally, for the transformation of glucose and sucrose in EtOH/H2O media, the poor EL/LA yield over CTATOS [C₃PrIm][OTf]-MONS12 is due to the lack of Lewis acid sites, which limits the transformation of glucose or sucrose to fructose.

3.2.2. Catalytic stability and reusability. The issue of the reusability and stability of immobilized BAIL catalysts has been an essential investigative theme for catalyst research in the field of biomass transformation. Under the harsh reaction conditions for catalytic transformation of biomass or biomass-derived platform molecules, immobilized BAILs may suffer from leaching into the reaction media because of the high solubility of BAILs in most of solvents; on the other hand, strong adsorption of hydrophilic by-products on the catalyst surface may also deteriorate the catalytic reusability. In the current [C₃PrIm][OTf]-MONSs catalyzed HMF ethanolysis reaction system, the color of the catalyst changes from white to light yellow after the reaction. However, the catalyst becomes dark brown after it catalyzes the HMF hydrolysis reaction, which is due to the formation of more humins during the complex HMF hydrolysis process. These humins strongly adsorb on the surface of [C₃PrIm][OTf]-MONSs, which results in difficulty in catalyst recycling. Therefore, the reusability and stability of the [C₃PrIm][OTf]-MONSs catalysts are evaluated in the HMF ethanolysis reaction system by using CTATOS [C3PrIm][OTf]-MONSs12 as the representative catalyst. After each catalytic cycle, the spent catalyst is recovered by centrifugation and then drying at 100 °C for the next cycle. As shown in Fig. 9a, the conversion of HMF reaches ca. 100% for each catalytic run after the CTATOS [C3PrIm][OTf]-MONSs12-catalyzed HMF ethanolysis reaction proceeds at 120 °C for 40 min; at the same time, the selectivity to EL slightly decreases from 42.7 (first run) to 42.4 (second run) and 38.5% (third run), while the selectivity to EMF increases somewhat from 48.9 (first



Fig. 9 Catalytic reusability of the representative *CTATOS* [C₃PrIm] [OTf]-MONSs12 in ethanolysis of HMF (a). Nitrogen gas adsorptiondesorption isotherm and pore size distribution curve (b) as well as the TEM image (c) of the three times spent *CTATOS* [C₃PrIm][OTf]-MONSs12. 0.278 mmol HMF, $n_{EtOH}: n_{HMF} = 248$, HMF-to-catalyst weight ratio of 1 wt/wt, 120 °C, 40 min.

run) to 49.8 (second run) and 51.5% (third run). Accordingly, the total selectivity of the catalyst to EMF and EL remains unchangeable (*ca.* 91.3%). Therefore, *CTATOS* [C₃PrIm][OTf]-MONSs12 exhibits good stability in HMF ethanolysis reaction, and the slightly decreased selectivity to EL is due to the loss of a small amount of catalyst powder, which may slightly decelerate the formation rate of EL. To account for the good catalytic reusability of *CTATOS* [C₃PrIm][OTf]-MONSs12, the textural properties and morphology of the three times spent *CTATOS* [C₃PrIm][OTf]-MONSs12 are tested. As shown in Fig. 9b, the three times spent *CTATOS* [C₃PrIm][OTf]-MONSs12 still displays well-defined sorption isotherms with the pore-condensation step occuring at $P/P_0 = 0.4$ -0.8; simultaneously, its mesopore size distribution is still centered at 3.8 nm, consistent with that of its original state;

however, its BET surface area and pore volume have somewhat decreased as compared with those of the fresh catalyst (551 m 2 g $^{-1}$ and 0.94 cm 3 g $^{-1}$ vs. 581 m 2 g $^{-1}$ and 1.13 cm³ g⁻¹, Table 1). From the TEM observation displayed in Fig. 9c, it is found that the three times spent CTATOS $[C_3$ -PrIm [OTf]-MONSs12 still maintains perfect spherical nanostructures with open interconnected mesopores, and the adsorption of by-products is hardly observed on the surface of the spent catalyst. The retention of excellent textural properties and perfect morphology of the spent catalyst ensures the good catalytic reusability; additionally, the hydrophobic microenvironment of the silica/carbon framework may avoid acid site deactivation due to strong adsorption of hydrophilic humin by-products.

Finally, the catalytic stability of CTATOS [C₃PrIm][OTf]-MONSs12 is tested by monitoring the leaching of the $[C_3PrIm]$ [OTf] group during the catalytic process. It shows that the Brønsted acid site density (873 μ eq g⁻¹) of the three times spent CTATOS [C₃PrIm][OTf]-MONSs12 is almost the same as that of the fresh catalyst. Additionally, the sulfur element coming from the [C₃PrIm][OTf] group is not found by ICP-OES determination in the reaction medium after three cycles of ethanolysis reaction. Both results indicate the excellent catalytic stability of CTATOS [C₃PrIm][OTf]-MONSs12. This is mainly attributed to the chemical interaction between the $[C_3$ -PrIm[[OTf] group and silica/carbon framework; additionally, [C₃PrIm][OTf] groups are confined within the abundant mesopores of organosilica nanospheres, which effectively avoids their leaching. Therefore, as-prepared [C₃PrIm][OTf]-MONSs can work as efficient and recyclable solid acid catalysts in biomass transformation.

4. Conclusions

Chemical immobilization of [C₃PrIm][OTf] on chloropropyl functionalized mesoporous organosilica nanospheres to prepare [C₃PrIm][OTf]-MONSs catalysts are realized via a liquid-interface assembly strategy in a weakly alkali O/W microemulsion system followed by successive chemical modifications with imidazole, 1,3-propane sultone and HOTf. The particle size and pore morphology of the catalysts can be adjusted by changing the co-hydrolysis and co-condensation time of organosilane precursors and the structure of the quaternary ammonium surfactant. Various [C3PrIm][OTf]-MONSs catalysts, regardless of their particle sizes and pore morphologies, all can transform HMF in EtOH media rapidly and completely, attributed to their superstrong Brønsted acidic nature and unique spherical nanostructure with abundant mesopores; however, the selectivity to EL strongly depends on the particle sizes and pore morphologies of the catalysts by controlling the diffusion distance of reactants and products, population of acid sites and accessibility of the acid sites. As for the transformation of HMF in water media, both conversion of HMF and selectivity to LA are remarkably dominated by the particle sizes and pore morphologies of the [C₃PrIm][OTf]-MONSs except for the superstrong Brønsted

acidic nature. Among the various $[C_3PrIm][OTf]$ -MONSs catalysts, *CTATOS* $[C_3PrIm][OTf]$ -MONSs12 with the smallest particle size, superior textural properties and 3D wormhole-like interconnected mesostructure shows the fastest HMF transformation rate and significantly improved accessibility for the reactants in both target reactions, which gives it the highest conversion of HMF and selectivity to LA and EL. The work suggests that the particle size- and pore morphology-controlled preparation of immobilized BAILs is an effective strategy to improve the catalytic activity and selectivity in transformation of HMF to valuable chemicals such as EL and LA.

Conflicts of interest

There are no conflicts to declare.

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